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strip in barrels, baskets or bulk... without electric current

metal stripper A A new alkaline compound that chemically dissolves nickel, copper, zinc, cadmium and silver from steel without etching or attack. The steel is clean and ready for refinishing. Suitable for rack, basket or barrel stripping. Removes excess silver solder from steel rapidly. Patents pending.

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Corrosion	Electrothermic
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Among the means to this end are the holding of meetings for the reading and discussion of professional and scientific papers on these subjects, the publication of such papers, discussions, and communications as may seem appropriate, and cooperation with chemical, electrical, and other scientific and technical societies.

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Editorial

New Editorial Appointments

WITH the retirement of Professor Uhlig as Editor after a distinguished career, it becomes necessary to make changes in the management of the JOURNAL. It is intended that the high standard of technical publication achieved under the retiring Editor shall be maintained and the volume published increased as the budget permits. With the larger number of papers presented before recent general meetings of the Society, greater selectivity can be exercised in publication. The resulting improvement in quality will attract, in turn, contributions from the ablest investigators in the broad field of electrochemistry. It is the responsibility of Professor Hackerman and his able staff of Divisional Editors to scrutinize and arrange for the review of all technical manuscripts. Professor King will be associated with the Technical Editor in this work.

A second function of the JOURNAL is the publication of news and information of current interest. In order to improve this section and provide the world coverage to be expected of the organ of an international society, Mr. Thomas, as News Editor, will have the assistance and collaboration of Regional Editors located in important areas of the United States, in Canada, Great Britain, and India. Contributions from these regional representatives should keep readers of the JOURNAL abreast of current affairs and developments in world-wide electrochemistry, in industrial, academic, and governmental circles. It is to be expected that copy from these sources will come to supplant some of the types of material which have appeared previously in the "Current Affairs" section. The space previously devoted to "Technical Notes and Reviews" will be used for publishing more technical papers and letters of technical nature addressed to the Editor. The latter are to be encouraged and will receive prompt attention. The last day of the month is the deadline for such letters, and their publication will take place a month and a day later.

Miss Reid, as Managing Editor, will continue to have charge of copy preparation, layout, and production—duties which she has discharged so skillfully during the past three years. Mr. LaQue will continue as Business Manager, and the new Chairman of the Publication Committee will exercise, insofar as necessary, the nominal duties of Editor.

—RMB

FUTURE MEETINGS OF

The Electrochemical Society

Detroit, October 10, 11, 12, and 13, 1951

Sessions on

Corrosion, Electrodeposition, Electro-Organic Chemistry

Round Table on Electrothermics

Headquarters at the Statler Hotel

* * *

Philadelphia, May 4, 5, 6, 7, and 8, 1952

FIFTIETH ANNIVERSARY MEETING

Sessions on

Electric Insulation, Electronics, Electrothermics

Luminescence, Rare Metals, Theoretical Electrochemistry

* * *

Montreal, October 27, 28, 29, 30, and 31, 1952

Headquarters at the Mt. Royal Hotel

* * *

New York, April 12, 13, 14, 15, and 16, 1953

Headquarters at the Statler Hotel

Papers are now being accepted for the fall meeting, to be held in Detroit. Abstracts (not exceeding 75 words in length) are due at the Secretary's Office, 235 West 102nd Street, New York 25, N. Y., *not later than August 1, 1951.* Complete manuscripts should be sent in triplicate to the Editor of the JOURNAL at the same address.

The Thermal Evaluation of Formvar Resin[1]

THOMAS D. CALLINAN

Naval Research Laboratory, Washington, D. C.

ABSTRACT

Deterioration of plastic insulation is a highly complex process influenced by many factors including time, temperature, plasticizer content, and changes both in molecular weight and in basic chemical character. Past methods of evaluation have, accordingly, been empirical ones using accelerated aging tests, but no method has been available for predicting the life of insulation under service conditions.

A critical evaluation is undertaken of the electrical properties of formvar resin, an insulant of proven superiority, and the values determined serve as a key to predicting the life of insulation in general. Data thus obtained are presented graphically for evaluating insulation found in practice.

INTRODUCTION

It is the purpose of this paper to present the results of a series of studies on the changes which certain vinyl polymers undergo at elevated temperatures and to establish from the data a nondestructive method of evaluating the life expectancy of an electrical insulant.

The reasons for using an insulating varnish in electrical apparatus are threefold: a varnish confers mechanical strength, electrical strength, and moisture resistance on the assembly. A material may be mechanically poor but electrically good, e.g., bentonite films, or vice versa, cement. Again a material may be mechanically and electrically good, but only when dry, e.g., cellulose paper. Any attempt then to correlate the characteristics of a dielectric with the life expectancy of the material must take cognizance of the mechanical, chemical, and electrical properties as a concatenated whole.

Previous Methods

The employment of dielectric strength as a measure of the suitability of an insulant suffers precisely from the lack of correlation with mechanical effects (1). "Both time and temperature have the effect of decreasing the mechanical strength of insulations, eventually resulting in its becoming brittle, and causing it to disintegrate. Class A insulation does not fail by electrical breakdown upon arrival of some critical temperature but by mechanical deterioration. Hence the electrical strength of insulation cannot be correlated with its mechanical strength" (2).

Other investigators (3), after assuring themselves of the suitable characteristics of a material, have studied the effects of impurities on the substance by changes in power factor or tensile strength. In some cases correlations have been found between the change in power factor with time and the life expectancy of the insulation. These are usually exceptional cases because the power factor, as a measure of loss, has meaning only when the dielectric constant does not change (4).

Tensile, compressive, flexural and abrasive strengths of materials have served as qualitative aids in evaluating new varnishes and adhesive coatings (5); they all suffer from the totally destructive character of the test.

EXPERIMENTAL METHODS

Properties of Polyvinyl Formal

The material employed for this work was a commercial polyvinyl formal[2] with the following properties (6):

TABLE I

Specific gravity	1.2–1.3
Refractive index	1.5
Heat distortion point	71°–77°C
Water adsorption	0.6–1.3 per cent
Solubility:	Soluble in tetrachlorethane and ethylene tetrachloride. Slightly soluble in dioxane and toluenebutanol. Very slightly soluble in the higher ketones. Insoluble in alkalies and hydrocarbons.

Tensile properties:

°C	Tensile strength	% Elongation
−30	12,000 psi	4
0	10,000	4
60	2,500	7
80	200	20

Dielectric strength:

1200–1600 volts per mil (vpm) 0.003 in. (0.008 cm) sample; short time; $\frac{1}{8}$ in. (0.3 cm) electrodes.

[1] Manuscript received May 1, 1950. This paper prepared for delivery before the Cleveland Meeting, April 19 to 22, 1950.

[2] Formvar (15/95) "E" produced by the Shawinigan Company.

Examination of these data indicates that the material suffers serious plastic distortion at 71°–77°C eventuating in it losing over 90 per cent of its tensile strength accompanied by a fivefold increase in elongation. Under such conditions the viscosity of the plastic has changed appreciably and an appreciable change in the electrical constants is to be expected. This is shown later in Fig. 1.

Preparation of Films

To 500 ml of Eastman tetrachlorethane, 28 g of Shawinigan Formvar "E" were added slowly with vigorous agitation at room temperatures. The dispersion was filtered through cheesecloth to remove the undissolved particles and then poured into a freshly cleaned, dry glass plate, 900 cm² in area. The solvent was permitted to evaporate overnight at room temperature. The plate with the tightly adhering film was then submerged in a pan of water, and after the film separated, it was dried between filter papers and permitted to come to room temperature at equilibrium conditions. Films prepared in this way were found to be 0.005 ± 0.0005 cm in thickness over an area of 300 cm². Microscopic examination at 430× indicated a fairly continuous pellicle having no birefringent particles or gelled areas.

Determination of Electrical Characteristics

A piece of aluminum foil 4 cm in diameter and 0.008 cm in thickness was covered on one side with a homogeneous section of a freshly cast and dried film and warmed slightly to permit the plastic to fashion itself snugly against the metal. A silver electrode 2.5 cm in diameter was then painted on the plastic from a dispersion of Du Pont No. 4113 silver paste in absolute alcohol. The composite was placed in an Elliott cell (7) and thoroughly dried at 105°C for two hours; the temperature was then lowered to −60°C by using a mixture of dry ice and isopropyl alcohol. The audio-frequency characteristics were determined on a General Radio 71C-AR capacitance bridge employing a Hewlett-Packard 200-BR oscillator as a frequency source and a General Radio 814-A amplifier for the RCA-155 oscilloscope used as a detector.

Data Obtained

Electrical Properties of Polyvinyl Formal

The variation of the dielectric constant of polyvinyl formal with temperature is shown graphically in Fig. 1. A rapid change in the dielectric constant ϵ' is observed in the region 70°–90°C, which is the same temperature range at which the viscosity of the plastic changes abruptly. The loss factor ϵ'' rises to a maximum corresponding to the primary absorption peak at the frequencies indicated on the curves. Incorporation of tricresyl phosphate in the film reduces the viscosity of the plastic appreciably, resulting in a shifting of the loss-factor maximum to lower temperatures; simultaneously a broadening of the curve is observed as shown in Fig. 2. Closer

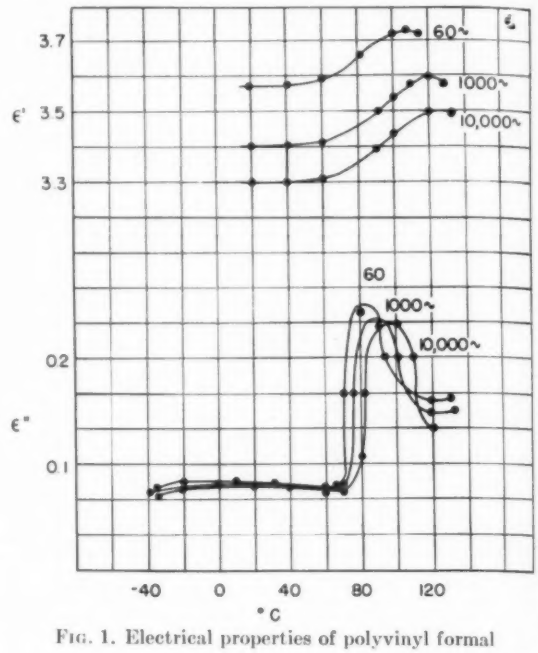

Fig. 1. Electrical properties of polyvinyl formal

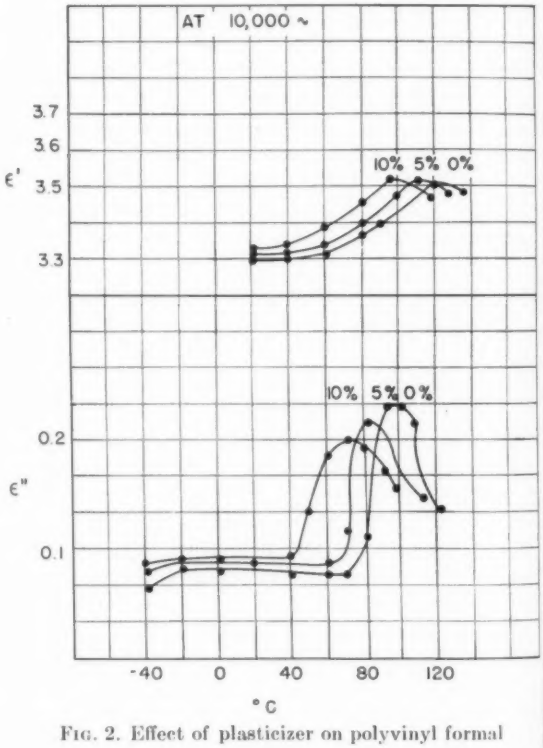

Fig. 2. Effect of plasticizer on polyvinyl formal

examination, as shown in Fig. 3, indicated that at lower temperatures and frequencies the losses tend to reach a maximum at about −20°C and that they

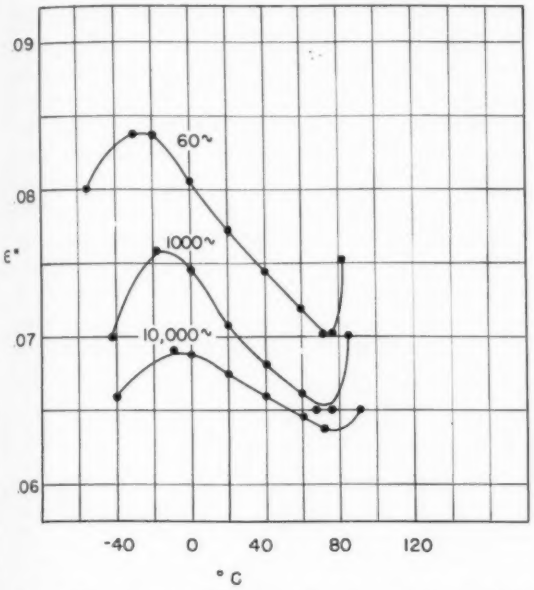

FIG. 3. Low temperature absorption in unaged polyvinyl

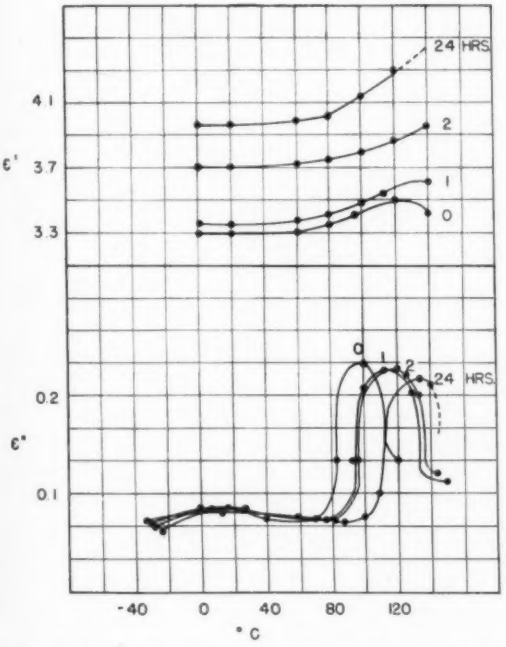

FIG. 4. Effect of thermal aging (175°C) on polyvinyl formal at 10,000 ~.

recede to a minimum at 72°C. This phenomenon has been described by Garton (8) as occurring in glycol-phthalate resins, and Kienle and Race (9) have noticed it in shellac and in polymerized glyptal. Garton failed to observe the absorption peak in rosin or in unpolymerized glyptal. Fuoss (10) has developed an explanation which was applied successfully by Busse (11) to the interrelation of mechanical and electrical properties of polyvinyl chloride. Methyl methacrylates also undergo this phenomenon (12).

Fuoss and others have found that the minimum loss-factor value corresponds to the brittle point or the internal melting point of the plastic. Such a point is of interest because it is a direct link between the mechanical and electrical properties of plastics. The brittle point-loss factor relationship has also been observed in cellulose (13).

Electrical Properties of Aged Films

The properties of the polyvinyl formal disclosed thus far are those of freshly cast films of the material. The effect of aging the pellicles over a period of 24 hours at 175°C in an air oven changes the value of these constants appreciably as shown in Fig. 4. The dielectric constant is seen to increase appreciably with aging and the position of the loss-factor peak is observed to shift to higher temperatures. Concomitantly the temperature corresponding to the minimum loss-factor point rises, indicating that the material remains in a nonplastic or embrittled state at higher temperatures. Since the life of an electrical insulation is related to the mechanical (14) embrittlement of the pellicle, the rate of change of the minimum loss-factor temperature is a measure of the life expectancy of the insulation. Any electrical test which can be correlated with this change in brittle point should be a measure of the life expectancy of the insulation.

The work of innumerable investigators (15) has shown that power factor determined under standard conditions results in, at best, a scattering of points. On the other hand, the determination of capacitance offers fewer interpretive difficulties. Fig. 4 indicates that there is an appreciable change in the dielectric constant with aging, as well as a change in loss factor. The low-temperature absorption peak also shifts markedly, as shown in Fig. 5, where the increase in the height of the curve is a measure of the loss of plasticizer or entrapped solvent. The simultaneous changes observed, viz., the increase in dielectric constant with age and the increasingly high value at which the internal melting of the plastic occurs, are shown graphically in Fig. 6.

Simultaneous Effect of Temperature and Plasticizer Content on the Dielectric Constant

Now the traditional treatment of the dielectric constant (and of the loss factor) has been to relate

measurements first to temperature and then to time and to consider the effects of these two factors independently. The result, as in the case of dielectric resistance and dielectric strength, has always been a series of highly variable curves relating, say,

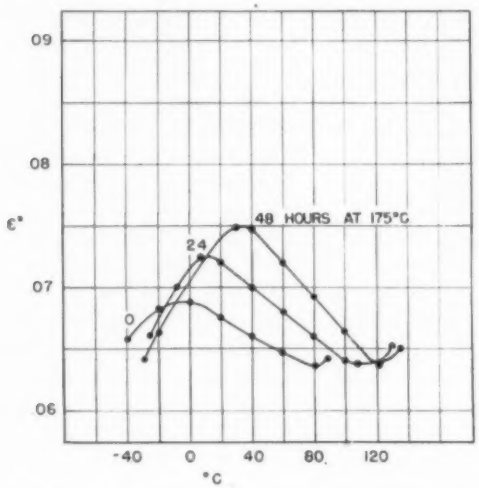

FIG. 5. Effect of aging on the low temperature absorption in polyvinyl formal at 10,000 ~.

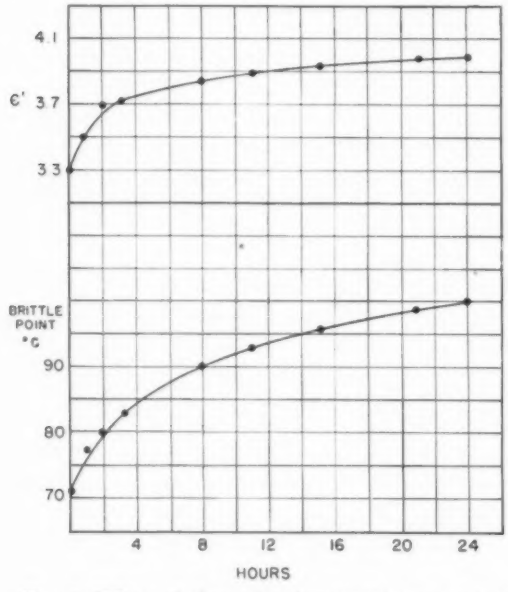

FIG. 6. Effect of thermal aging (175°C) on polyvinyl formal.

the value of the dielectric constant to temperature, either for a plastic containing a given proportion of plasticizer or for a known plastic composition after a given lapse of time. But accurate extrapolation of these curves is not possible and they are apparently lacking in correlation. If, on the contrary, a three-dimensional curve be fitted to the experimental data, it turns out to be a smooth but complex surface of the type shown in Fig. 7.

It is seen at once that three types of curves (depending upon the temperature of test) may be obtained when a section is taken in the *YZ*-plane, that is, when the dielectric constant is plotted against time (or plasticizer evaporation) at a fixed temperature. Two are hyperbolic functions while the third is describable by a cubic equation having two imaginary roots (16). At relatively low temperatures, the dielectric constant falls off hyperbolically with time, while at somewhat higher temperatures the value rises. At some intermediate temperature, the curve of dielectric constant vs. time shows a maximum. Yet at extremely high temperatures, surprisingly, the curve shows a minimum. This being the case, there is little wonder that the collection of experimental values of the dielectric constant has led to confusion.

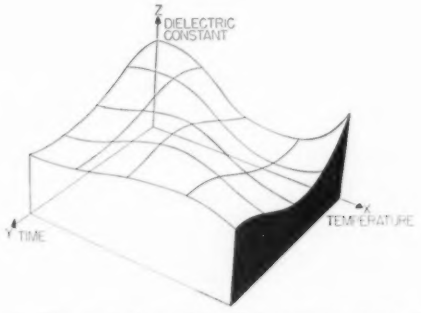

FIG. 7. The variation of the dielectric constant of polyvinyl formal with temperature and plasticizer content (converse of time).

Dielectric Loss Factor vs. Temperature vs. Plasticizer Content

In a manner analogous to that developed in Fig. 7, a companion surface has been prepared indicating the variation of dielectric loss factor with temperature and with plasticizer content, Fig. 8. The magnitude of the change which the dielectric loss factor undergoes on being subjected to heat is remarkable. As plasticizer is added to the polyvinyl formal the distinctness of the peaks disappears until finally only a gentle but rising slope is observed at high concentrations. Similarly it may be demonstrated that violent changes are undergone when the test-temperature is held constant and the plasticizer is evaporating.

Effect of Plasticizer Content and Temperature on the Mechanical Properties of Polyvinyl Formal

While extensibility, stretch, or elongation is used for test purposes as a means of evaluating the me-

chanical properties of plastics, the employment of Young's modulus is technically more accurate. Thus the failure of the plastic film being mechanical, the mechanism may be considered to have arisen due to the displacement of a particle of matter by an "unrecoverable" amount. This displacement accounts for the plastic's ability to be distorted without rupture under heavy vibrational loads; the concept also explains why a material may have an apparently zero elongation and still not fail as an

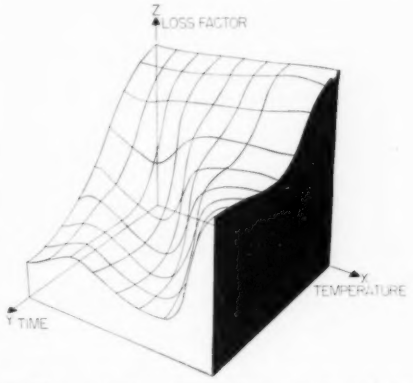

FIG. 8. The variation of the dielectric loss factor with temperature and plasticizer content (converse of time).

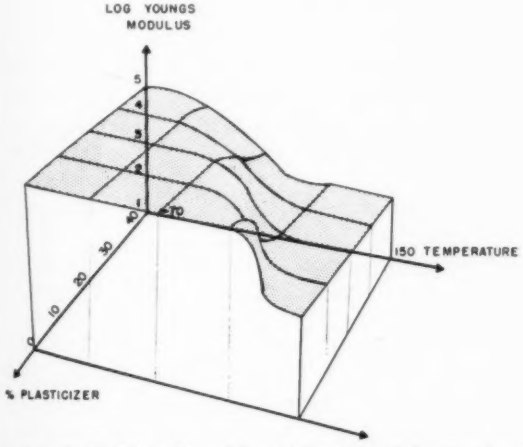

FIG. 9. Relationship of log Young's modulus vs. temperature vs. plasticizer content.

electrical insulator. Unless the material is stressed mechanically beyond its recovery limit the plastic dielectric should remain an insulator.

The effects of temperature and plasticizer content on polyvinyl formal were studied by constructing surfaces based on the experimental data. Fig. 9 presents graphically the effect of temperature and plasticizer content on the modulus of elasticity of the material. The familiar cut shows the gentle slope of the polyvinyl formal as it is warmed and its modulus of elasticity falls. While the change as shown in the figure is not much, the reader is cautioned that the height of the block is to be evaluated as the logarithm of the modulus of elasticity.

At low temperatures all the materials, whether or not plasticizer is present, have high moduli (and tensile strength). As the temperature rises those having the highest concentration of plasticizer suffer mechanical distortion first and finally as the compositions containing less plasticizer are studied high temperatures are required for distorting them. The abrupt drop in the height of the model appearing in the center of the picture corresponds to the mechanical brittle temperature of polyvinyl formal containing no plasticizer.

Application of the Data

Keeping in mind the original requirement that the method for evaluating the state of insulation must be nondestructive, it would appear that, if a temperature could be found on any one of the electrical characteristics vs. time plots where a very definite and absolute change can be detected and which at the same time can be related to the mechanical embrittlement of the plastic, a solution might be obtained. Surprisingly, examination of the data reveals that the greatest change, Fig. 8, occurs in the dielectric loss factor vs. time curve when examined at the brittle point. This corresponds also to a test-temperature at which the modulus of elasticity vs. time curve also suffers an abrupt change, Fig. 9.

In short, it appears that a definite and abrupt change in the dielectric loss factor of polyvinyl formal on aging when studied at its brittle point can be related to the mechanical condition and hence the life expectancy of the insulation.

Any discussion of this paper will appear in a Discussion Section, to be published in the December 1951 issue of the JOURNAL.

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The Origin of Multiple Bands in Luminophors Activated by Divalent Manganese[1]

F. A. Kroeger and P. Zalm

Philips Research Laboratories, Eindhoven, Holland

ABSTRACT

An examination of the theories proposed to explain the appearance of multiple bands with manganese activated luminophors indicates that the "cluster" theory is to be preferred to the "coordination" theory. It is probable that the fluorescent bands are due to transitions from various excited states to one single ground state. The variation of fluorescence with temperature is discussed on the basis of this model and the assumption that several bands originate in one center.

The Atomic Configuration of Centers in Luminophors Activated by Mn^{2+}

All luminophors containing divalent manganese as activator show a fluorescence varying from green to infrared which must be ascribed to electronic transitions in the manganese ions. The energy levels between which the transitions take place depend on the surroundings; the strength and the symmetry of the local lattice field play an important part, but other effects, as for instance, interaction between neighboring activator ions, may not be neglected. In several systems various bands occur simultaneously. In glasses activated by manganese (1) and in $(Zn,Be)_2SiO_4$-Mn(2, 3, 4) and $(Zn,Be)_2GeO_4$-Mn(4, 5), for instance, the fluorescence consists of green, yellow, and red bands, while in $MgSiO_3$-Mn and Mg_2SiO_4-Mn red and infrared bands occur (6). With Zn_2SiO_4-Mn having a normal activator content, the fluorescence is green, but at low temperatures, a red band appears in addition with products having an exceptionally large (20%) manganese content (2).

The appearance of several bands, in particular, green and red ones, has been explained by Linwood and Weyl (1) on the basis of the assumption that the spectral distribution of the fluorescence is mainly determined by the number of anions adjacent to the activator (coordination number). Assuming that the activator is present at normal lattice sites and replaces the corresponding cations of the matrix lattice, and correlating the coordination numbers 4 and 6 of zinc and magnesium in Zn_2SiO_4 and Mg_2SiO_4 with the green and red fluorescence shown by these substances when activated by manganese, the rule was formulated that a high coordination number corresponds to a long-wave fluorescence, and vice versa. With glasses, in which the coordination is not strictly uniform, this theory could be applied without meeting serious difficulties. When trying to apply it to Zn_2SiO_4-Mn, however, the red band appearing at high manganese concentrations could only be explained by an additional assumption. In this structure, both zinc and silicon have a coordination four, and manganese at such sites should give a green band. Positions with a higher coordination are those that are normally not occupied (interstitial sites); the red was attributed to manganese at such sites. In simple structures, the occupation of interstitial sites is accompanied by the formation of an equal number of unoccupied lattice sites (Frenckel defects). In more intricate lattices of the type discussed here, the occupation of interstitial sites may also become possible by a simultaneous replacement of highly charged cations by cations of a lower charge; in this case by the replacement of Si^{4+} by Zn^{2+}, Be^{2+} or Mn^{2+} [Schulman (3, 5)]. As the small beryllium ions seem to be particularly suitable for this function, it was suggested that the appearance of a red band in $(Zn,Be)_2SiO_4$-Mn might be explained in this way, and that with Zn_2SiO_4-Mn, the larger Zn^{2+} and Mn^{2+} ions might take over this function, although to a smaller extent.

Any theory for the multiple bands in manganese activated luminophors must be able to explain the variation of the red:green ratio with manganese concentration. As outlined above, the coordination theory encounters certain difficulties in explaining the fact that this ratio increases with increasing manganese concentration, as we believe is shown by the following arguments.

In the model proposed by the coordination theory, the proportion between red and green in the fluorescent spectrum is determined by the distribution of manganese over normal and interstitial lattice sites. The number of manganese ions to be found at normal lattice sites is, to a first approximation, a linear function of the concentration,

$$n_{\text{green}} \sim C_{\text{Mn}}. \qquad \text{(I)}$$

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For Linwood and Weyl's original version of the theory the number of manganese ions to be found at interstitial sites will be at most also linearly dependent on the manganese concentration,

$$n_{red} \sim C_{Mn}. \qquad (II)$$

This leads to a red:green ratio which is independent of the manganese concentration. As the incorporation of manganese at interstitial sites is accompanied by the formation of cation vacancies, however, it is likely that the relative solubility of manganese in the interlattice will decrease with the concentration. This possibility leads to a red:green ratio actually diminishing with increasing manganese concentration, contrary to what is observed.

In the theory proposed by Schulman, the number of manganese ions at lattice sites is not changed, (I) remaining valid. The number of manganese ions at interstitial sites is now, however, proportional to the product of C_{Mn} and C_R, where C_R is the concentration of Si^{4+} ions which have been replaced by Zn^{2+}, Be^{2+}, or Mn^{2+}. If the probability of replacing Si^{4+} is the same for each of the three kinds of ions, then C_R is independent of the relative concentration of these ions and therefore also of the manganese concentration. Accordingly,

$$n_{red} \sim C_{Mn}. \qquad (III)$$

Together with (I), this again leads to a constant red:green ratio. Now if Si^{4+} is replaced preferentially by Zn^{2+} or Be^{2+}, C_R is proportional to the concentration of these ions. As $C_{Zn} + C_{Be} + C_{Mn} = 1$, this means that $C_R \sim (1 - C_{Mn})$ and accordingly

$$n_{red} \sim C_{Mn}(1 - C_{Mn}). \qquad (IV)$$

Together with (I), this leads to a red:green ratio decreasing with increasing manganese content. Finally, if Si^{4+} is replaced preferentially by Mn^{2+}, C_R is proportional to the manganese concentration, and therefore

$$n_{red} \sim C^2_{Mn}. \qquad (V)$$

Only in this case does the red:green ratio increase, as it should, with increasing manganese content.

In our opinion, this last possibility is rather improbable. In Zn_2SiO_4-Mn in which only Zn^{2+} and Mn^{2+} are present, replacement of Si^{4+} will occur predominantly by the smaller Zn^{2+} ions. The same argument holds *a fortiori* for Be^{2+} in $(Zn,Be)_2SiO_4$-Mn. It therefore appears to us that unless the coordination theory is combined with additional features, it does not account for the variation of the red:green ratio. Schulman (5) and Linwood and Weyl (1) have, in fact, proposed such a combination in suggesting the effect of concentration quenching in addition to that of coordination.

While such a combination presents a self-consistent picture as far as the red:green ratio is concerned, there are certain other points which appear to present difficulties to any theory which involves the idea of interstitial manganese being responsible for the red band, and of manganese at normal sites for the green. If this be so, an excess of ZnO above the stoichiometric amount should favor the red emission since it favors the incorporation of Mn in the interlattice[2]. On the other hand, an excess of SiO_2 should favor the incorporation of Mn at lattice sites and thus favor the green emission. Neither of these effects are found experimentally. A second point is concerned with the absence of a red band in Zn_2GeO_4-20 per cent Mn_2GeO_4 although such a band does occur in the corresponding silicate (5)[3]. Although this difference presents certain difficulties to any theory which may be proposed to explain the effects concerned, we believe it is especially hard to explain on the basis of the coordination theory. Whenever relatively large divalent ions are to replace smaller tetravalent ions, as is assumed in this theory, they will do so to an extent which is the greater the larger the tetravalent ions. Therefore the effect should be stronger with germanates than with silicates, contrary to what is indicated by the experiments.

We will now proceed to a consideration of the cluster theory, originally proposed by Maurer (7) for $MgSiO_3$-Mn and Mg_2SiO_4-Mn and by one of the authors (8) for Zn_2SiO_4-Mn and $(Zn,Be)_2SiO_4$-Mn. This model is based directly on the observed concentration dependency of the red:green ratio. It is assumed that all manganese ions are situated at normal lattice sites, but that some of them are isolated, having only zinc ions at adjacent cation sites, while others have one or more other manganese ions at these sites. In the original theory, the iso-

[2] Schulman (5) found in the case of $(Zn,Be)_2GeO_4$-Mn that Be in excess of the amount corresponding to the solubility limit of Be_2GeO_4 in Zn_2GeO_4 still promoted the emission of the red band. This can be explained, as was done by Schulman, on the basis of the coordination theory. We believe, however, that an effect of coordination (i.e., Mn at interstitial positions) is not necessarily involved. It may well be that, in this case, part of the Be^{2+} replaces Si^{4+} with the formation of O^{2-} vacancies. We would then be dealing with $(Zn,Be)_2GeO_4$-Zn_2BeO_3 mixed crystals which may have a different fluorescence spectrum due to manganese ions at lattice sites next to Be^{2+} or next to an O^{2-} vacancy. The effect is, of course, not the sort of effect we discussed above, in which a stoichiometric excess was involved.

[3] These results have been confirmed by experiments in our laboratory, in which the measurements were extended to 20°K.

lated activator ions were assumed to be responsible only for the short-wave bands, the clusters only for the long-wave bands[4]. In view of recent experimental work, however, we have come to the conclusion that the effect of clusters is more complex than this. It has been shown by various authors (11), for example, that the emission spectrum of $(Zn,Be)_2SiO_4$-Mn can be analyzed into at least five distinct sub-bands[5] while even the spectrum of $Zn_2SiO_4 - 10^{-3}Mn_2SiO_4$ is found to consist of two sub-bands (12). Furthermore, it has been shown that the green band appearing in Zn_2SiO_4 containing large amounts of manganese (20%) is not simply the green band found at lower concentrations. The two bands differ principally in that the transitions responsible for them have different transition probabilities. The cluster theory, however, requires that the former green band originates from an aggregate of Mn ions and the latter green band from a single Mn ion. We are thus led to believe that a cluster can give rise not only to bands of longer wavelength but also to new green bands.

The fact that the two green bands, one originating in a cluster and the other in a single Mn ion, differ principally in that the transitions responsible for them have different transition probabilities, gives a clue as to how clustering may operate in changing the emission spectrum. The appearance of new bands may be due either to a shift of one band, caused by a variation in the energy separation between the levels involved, or by a variation in the relative magnitude of transition probabilities for transitions between levels which are always present at approximately the same energy. The experimental facts indicate that the latter possibility is realized. We therefore picture the single excited Mn ion as being capable of several transitions in a manner similar to that already worked out in considerable detail by Butler (11). The effect of clustering is then to alter the relative transition probabilities of the various possible transitions. Thus, for example, a singlet Mn ion may fluoresce green because the green transition has the highest transition probability; a doublet may have a red fluorescence because these transitions have the highest probability, and a triplet may again fluoresce green because this transition probability has now become the highest. In this way the various sub-bands attributed to the Mn fluorescence can be accounted for, as well as the effect of clustering in changing the emission spectrum. While we have not made a detailed experimental correlation between the various sub-bands and the corresponding transition probabilities, we believe the above presents a consistent picture.

Support for the cluster theory is also found in other directions. It would be expected that, for a given system, association of the clusters should increase toward lower temperatures and dissociation toward higher temperatures. This is actually indicated by recent results of Jones (19) who studied the influence of the thermal history on the fluorescence of zinc-beryllium silicate activated by manganese. He found that quenching from a high firing temperature favors the green emission, in accordance with the above expectation[6]. The cluster theory is also supported by magnetic measurements with ZnF_2-MnF_2 (9) in which the presence of manganese clusters is indicated by deviations from additivity. Schulman and coworkers (5) have estimated by simple statistical methods the concentration of clusters as a function of manganese concentration and found some correlation with the red:green ratio. Complete confirmation of the cluster theory in this direction, however, awaits a detailed knowledge of how clustering affects the fluorescent emission.

Two important experimental facts which must be accounted for by any theory are the effect of beryllium in promoting red bands in zinc silicates and germanates containing manganese, and the lack of red bands in Zn_2GeO_4 containing large amounts of manganese. In connection with the former, the effect of beryllium on the basis of the cluster theory must consist in the promotion of the formation of clusters; a direct influence of the beryllium as assumed previously (8, 10) can be excluded as this would result in an effect independent of the manganese concentration. The promotion of the formation of clusters can be explained as follows. Mn^{2+} is larger than Zn^{2+}, but Be^{2+} is smaller. When Be^{2+} and Mn^{2+} agglomerate, that is, occupy neighboring cation sites, the excess of volume of the large Mn^{2+} is partly compensated by the lack of volume of the small Be^{2+}. The resulting situation contains less strain than that in which Be^{2+} and Mn^{2+} are far apart. This effect therefore acts as an attraction between these ions. This argument does not hold for just one neighbor but for more as well. In this way, Be^{2+} tends to assemble several Mn^{2+} ions at

[4] In a recent paper, Schulman, Ginther, and Klick (21) have adopted this model to explain the appearance of a new emission band with $CaSiO_3$-Pb at high concentrations of lead.

[5] For the sake of simplicity, we have talked mainly of red and green bands throughout this paper. There is, however, nothing in our arguments which will not apply as well to a larger number of bands.

[6] The fact that he found that refiring at a lower temperature also favored the green, although to a smaller extent, must be attributed to a different effect, *viz.*, the separation of Be_2SiO_4 at the lower temperatures. This must be expected because the amounts of BeO present in Jones' samples exceed the limit of solubility and, according to Fonda (20), the solubility of Be_2SiO_4 decreases with decreasing temperature.

adjacent sites and in doing so forms Mn^{2+} clusters. In connection with the lack of a red band in the Zn_2GeO_4-Mn_2GeO_4 system, we have only to remember that the fluorescence due to a particular cluster is very sensitive to outer conditions. Thus a cluster which gives rise to red in the silicate may well give rise to green in the germanate.

The Term Scheme of the Manganese Centers

For compounds of divalent manganese, magnetic measurements indicate that the ground state of Mn^{2+} is $^6S_0$. Recent work of Johnson and Williams (9) proves that the same is true of Mn^{2+} in ZnF_2-Mn; the long-lived excited state from which the manganese fluorescence takes place is found to have a lower multiplicity. It has usually been assumed that the various fluorescent bands correspond to transitions from various excited states to the single ground state (14). Recently Fonda (15) has proposed a new picture in which the green and red bands are attributed to electronic transitions from one excited state to two lower levels, one being the actual ground state and the other a level slightly above it. This picture was based on an observation that the decay of the red and green bands in $(Zn,Be)_2SiO_4$-Mn was found to be identical (16). For such a model, however, not only the decay of the fluorescence but also the probability of radiationless transitions leading to quenching is identical, and therefore the green and red should be quenched at exactly the same temperature, contrary to what is observed (1, 8, 13, 15). Furthermore, measurements by Kroeger and Hoogenstraaten (13) indicate that the decay constants of the green and red sub-bands in $(Zn,Be)_2SiO_4$-Mn generally are not equal and the same was recently found by Schulman, *et al.* (23), Gergely (24), and Nagy (25). Therefore it seems that we must adhere to the old model.

A further argument in favor of the old model is obtained from absorption and excitation data. If the fluorescence bands correspond to electronic transitions to the ground state, then the reverse transitions must occur in absorption. (According to the Franck-Condon principle, the absorption bands to be expected must be displaced toward shorter wavelengths over a distance of the order of the width of the fluorescence band.) In the other model, however, only absorptions corresponding to the short-wave band are to be expected, the transition corresponding to the long-wave band starting from the higher and consequently less populated state. The first situation is found to be realized; the red band of $(Zn,Be)_2SiO_4$-Mn can be excited by wavelengths up to at least 5300 Å (2). Due to the fact that the transitions are forbidden, as is indicated both by the long lifetime of the excited state and by the variation in multiplicity accompanying excitation (9), the absorption and excitation bands concerned are extremely weak.

Our picture of the fluorescence of manganese centers involves the idea that several different bands may originate in one center. The character of the fluorescent emission from this center will depend on all the properties of the levels responsible for the bands. So far we have spoken principally of the transition probabilities for fluorescent emission. In addition there may be radiationless transitions from the various levels whose relative probabilities will affect the emission (13, 17). Also quenching via lattice states may affect one or another of the fluorescent transitions preferentially (13). Another possibility is that the actual positions of the levels may be affected, for example, by temperature changes (12). The situation is further complicated by the fact that several different types of centers (our theory supposes these to be singlet, doublet, etc., Mn ions) may exist simultaneously in the same fluorescent material. For example, two green bands which have quite different and independent decay rates may be emitted simultaneously from two different types of centers (13). With all these possibilities, it is obvious that the resulting fluorescent phenomena may be quite complex. As illustrations, we will consider two simple cases assuming the presence of one type of center only.

For simplicity we will speak of two excited levels in each center although the arguments apply as well to cases where each center has many excited levels. We will consider that radiationless transitions are of importance only between the two levels. In one case the separation between the two levels is assumed to be large compared to the thermal energy, kT. If, now, excitation is to the higher level only, the relative intensities of the two bands emitted will be determined simply by the relative magnitudes of the transition probabilities for the short-wave fluorescence, γ_g, and for the radiationless transition, β, from the higher to the lower excited state. As γ_g is nearly constant, while β will increase with temperature (as is normal for radiationless transitions), this will result in a relative increase of the long-wave fluorescence as the temperature increases. If β is much greater than γ_g, only the long-wave band is emitted. Furthermore, two distinct decay rates will be observed and the color of the emission will change during decay. In the other case the separation between the two levels is assumed to be of the same order as kT so that the populations of the two levels are maintained in thermal equilibrium. They will remain so during decay if, as is usual, the transition probabilities of fluorescence

are sufficiently small. An increase of the temperature now causes an increase of the relative intensity of the short-wave band. As will be explained below, a single decay rate will now be observed and the color of the emission will not change during decay.

Examples of the first case are not known. For the second case an example has been provided by Vlam (12) who observed a shift with increasing temperature in the relative intensity of two green bands in Zn_2SiO_4 - $10^{-3}Mn_2SiO_4$, corresponding to that predicted for this case. Here the manganese concentration was so low that clustering was probably not a factor and Vlam's silicate presumably contained one type of center only. The fact that a single decay rate has been observed (13) for Zn_2SiO_4 with low manganese content is also consistent with the predictions of the second case. Experimental evidence for the presence or absence of multivalued decay rates for the green emission from samples containing a higher concentration of manganese (5 mole %) is contradictory [see Klick and Schulman (26)]. We suggest that the discrepancies may arise from varying methods of preparation of the samples which may influence clustering and hence the presence or absence of more than one type of center.

It is evident that neither of the two illustrative cases apply to the red and green emission from manganese-activated Zn_2SiO_4 and $(Zn,Be)_2SiO_4$, since here different decay rates are observed for the red and the green, but the long-wave emission decreases with increasing temperature. This behavior must be explained by red and green originating in different centers, with different transition probabilities for the fluorescence transitions and also different values of the constants δ and ϵ which describe the nonradiative transitions (13) according to

$$\delta = \delta_0 e^{-\epsilon/kT}$$

The second illustrative case, where thermal equilibrium exists between the populations of the various excited levels, has been discussed in considerable detail by Kroeger and van den Boomgaard (22). If the equilibrium involves a Boltzmann distribution, then the decay of the fluorescence starting from each of our two assumed levels is identical and is given by

$$\bar{\gamma} = \frac{g_1\gamma_1 + g_2\gamma_2 e^{-\epsilon/kT}}{g_1 + g_2 e^{-\epsilon/kT}}$$

Here g_1 and g_2 indicate the statistical weights of the levels 1 and 2 while γ_1 and γ_2 indicate the transition probabilities of the fluorescence transitions starting from these levels. ϵ is the energy difference between the two levels. With increasing temperature, the contribution of γ_2 increases relative to that of γ_1 and, if $\gamma_2 > \gamma_1$, the measured decay constant γ therefore also increases. This explains the slight increase with temperature of the decay rate of sub-bands with a purely exponential decay as observed with Zn_2SiO_4-Mn in the temperature range in which dissipative transitions are still negligible (13).

Summary

The two principal theories which have been advanced for the explanation of the appearance of multiple bands with manganese activated luminophors, particularly the silicates and germanates, are the "cluster theory" and the "coordination theory." The former accounts quite naturally for the dependence of the red:green ratio on the Mn concentration, whereas the coordination theory requires both the effect of coordination and concentration quenching (or possibly some other factor) for a self-consistent picture. On the other hand, the effect of Be in promoting the red emission is quite naturally explained by the coordination theory, whereas the cluster theory requires an additional postulate concerning the effect of Be in promoting clusters. Taking these and other considerations into account, the cluster theory seems to present the simpler and more satisfactory picture.

In the cluster theory, the variation of luminescence observed is attributed to the interaction between manganese ions belonging to clusters and it seems that this influence must affect mainly the lifetime of the various excited states. It seems probable that the fluorescence bands are due to electronic transitions from various excited states to one single ground state and that several different bands may originate in one center. The variation of fluorescence with temperature can be explained on the basis of this picture.

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Any discussion of this paper will appear in a Discussion Section, to be published in the December 1951 issue of the Journal.

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The Electrochemical Behavior of Aluminum

II. In Solutions of Iron Sulfate[1]

J. V. Petrocelli

The Patent Button Company, Waterbury, Connecticut

ABSTRACT

A study has been made of the reactivity of pure aluminum with iron sulfate in solutions of varying acid strength. Electrode potentials, weight loss data, and polarization curves are presented, and it is shown that the reaction may be interpreted from an electrochemical point of view. The analysis of the behavior is based on the previously developed theory of the "mixed potential."

Introduction

The work reported in this communication is part of a general investigation on the electrochemical behavior of aluminum in solutions containing oxidation-reduction systems (1). The present study involves solutions of iron sulfate with various concentrations of sulfuric acid. The experimental approach and the interpretation of the results is strongly guided by the theory of the "mixed potential," which has already been treated in some detail (1).

Experimental

Materials and Apparatus

Pure aluminum (99.99) in the form of rolled sheet (0.25 mm thick) was used throughout. The compositions of the solutions, which were made with reagent grade chemicals and redistilled water, are given in Table I. The apparatus used and the experimental conditions were identical to those given previously (1).

Procedure

The aluminum was polished with #0000 paper using a kerosene paraffin mixture, cleaned in a hot mixture of alcohol and acetone and then in redistilled water. Great care was taken not to leave any abrasive particles imbedded in the surface. All but a defined area of about 1.0 to 2.0 cm² was coated with an insulating lacquer.

In general, an aluminum specimen was placed in the solution concerned and the potential recorded on open circuit until a fairly steady state was reached. The aluminum was then polarized by the application of an external current, designated as I. Then in order to obtain the limiting diffusion current density of the oxidation-reduction system on an inert electrode, a platinum electrode was substituted for the aluminum and polarized as previously described (1). In several cases the weight loss of the aluminum while on open circuit was obtained; this is reported in terms of current density and designated as i_0. The values of the electrode potentials are given with reference to the saturated calomel electrode.

Results

Time-Potential Behavior and Reactivity

On immediate immersion, the potential of aluminum was very cathodic and then changed rather rapidly to more anodic values becoming fairly steady in about 20 minutes. The general behavior is shown in Fig. 1. The steady state potential, on open circuit, was constant to within a few centivolts for any one specimen, while variations of about ±0.05 v were obtained with different specimens.

For any given concentration of H_2SO_4 there is a tendency for the open circuit potential to become more cathodic as the concentration of iron(III)-sulfate increases. This tendency is shown by the curve in Fig. 2. Increasing the H_2SO_4 from 0.5M to 5.0M while keeping the iron(III)-sulfate at 0.10M caused the open circuit potential to vary from about −0.4 v to about −0.3 v, thus becoming more cathodic with increase in acid strength. Increasing the temperature from 25° to 50°C in solution 2 did not effect the open circuit potential appreciably.

The rate of dissolution of aluminum, as obtained from the polarization curves and checked by weight loss measurements, showed a tendency to increase with increase in the concentration of iron(III)-sulfate, for a given acid strength (Fig. 2). Keeping the iron(III)-sulfate at 0.10M and varying the H_2SO_4 from 0.5M to 5.0M caused the reactivity to increase from 0.1 to 0.3 ma/cm². In solutions 10 through 13 which did not contain H_2SO_4 the rate of dissolution was equal to or less than 0.05 ma/cm². The reactivity increases with temperature; thus in solution 2, increasing the temperature from 25° to 50°C caused i_0 to increase from 0.1 to about 1.7 ma/cm².

[1] Manuscript received August 24, 1950. This paper prepared for delivery before the Buffalo Meeting, October 11 to 13, 1950.

Evolution of gas was never observed on the surface of aluminum while on open circuit.

TABLE I. *Composition of Solutions*

Solutions	$Fe_2(SO_4)_3$ moles/l	$FeSO_4$ moles/l	H_2SO_4 moles/l	pH
1	0.01	0.0	2.5	—
2	0.10	0.0	2.5	—
3	0.20	0.0	2.5	—
4	0.30	0.0	2.5	—
5	0.50	0.0	2.5	—
6	0.0	0.50	2.5	—
7	0.10	0.0	0.50	—
8	0.10	0.0	4.0	—
9	0.10	0.0	5.0	—
10	1.0	0.0	0.0	0.96
11	0.10	0.0	0.0	1.6
12	0.05	0.0	0.0	1.9
13	0.01	0.0	0.0	2.3

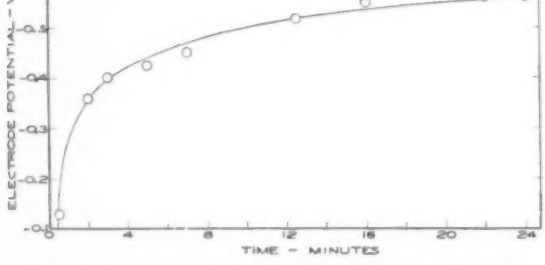

FIG. 1. Time-potential relationship in iron sulfate solution 1 at 25.0°C.

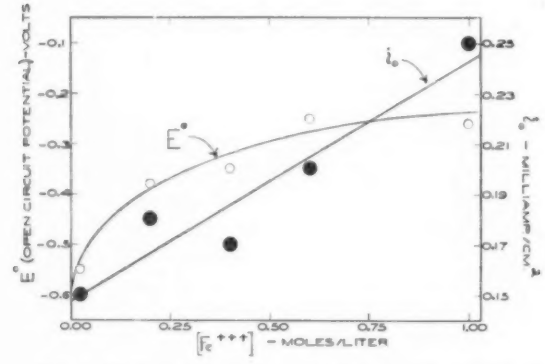

FIG. 2. Electrode potential and local action current on open circuit as a function of the iron(III)-sulfate concentration in solutions 2.5*M* in H_2SO_4.

External Polarization

Many specimens were subjected to anodic and cathodic polarization by means of an external current, and an analysis of the polarization curves was made by using the concepts of the mixed potential theory (1). In this manner the total or "real" cathodic current density, i_c, for the reduction of iron(III)-sulfate was obtained and the relation between the electrode potential and i_c determined.

Typical external polarization curves are shown in Fig. 3. The cathodic portion corresponds to the wave for the reduction of the ferric ion; the anodic portion shows a continuation of the same wave and an upper linear section. When this linear section is extrapolated back to the potential axis, the resulting line is practically identical to the anodic polarization curve of aluminum in H_2SO_4 of the same strength, and may be considered as the E versus i_a curve. The value of the current on the extrapolated portion corresponding to the open circuit potential is equal to i_0, the rate of dissolution on open circuit.

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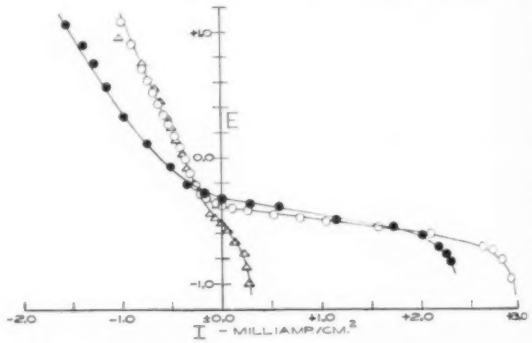

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It was found that the polarization curve for the reduction of iron(III)-sulfate depends upon the manner in which the aluminum is externally polarized. If the polarization is started while the aluminum is on open circuit or at more cathodic potentials, and one proceeds to the top of the curve and then, without interrupting the current, comes back down the curve, it is found that the two curves are not coincident. The "hysteresis" effect is shown in Fig. 4 where the curve obtained coming down lies at more cathodic potentials.

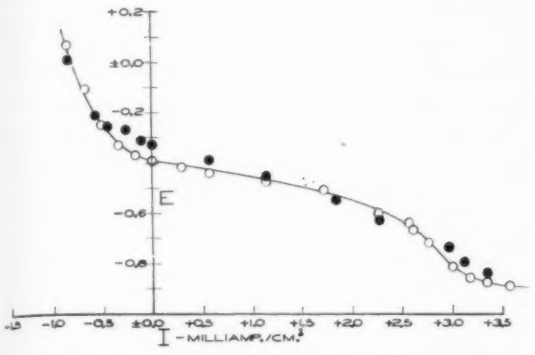

FIG. 4. External polarization curve for aluminum in iron(III)-sulfate showing the "hysteresis effect." ○-polarized from + 0.2 v to −0.9 v; ●-polarized from −0.9 v to +0.2 v.

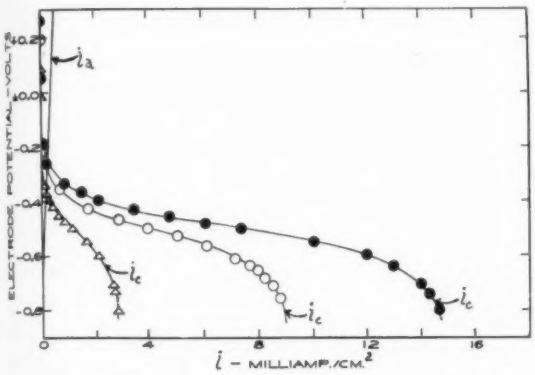

FIG. 5. The "real" polarization curve for the reduction of iron(III)-sulfate on aluminum, E versus i_c; and the self-anodic polarization of aluminum, E versus i_a. △-solution 2; ○-solution 4; ●-solution 5.

TABLE II.

Soln.	$Fe_2(SO_4)_3$ moles/l	H_2SO_4 moles/l	Temp °C	$(i_c)_d$ on Al ma/cm²	i_d on Pt ma/cm²	b volts	$E_{\frac{1}{2}}$ volts	pH
1	0.01	2.5	25	0.30	0.29	0.17	0.5	—
2	0.10	2.5	25	3.0	—	0.15	0.5	—
4	0.30	2.5	25	9.1	10.4	0.16	0.5	—
7	0.10	0.5	25	3.9	4.3	0.13	0.6	—
8	0.10	4.0	25	2.7	—	0.17	0.5	—
9	0.10	5.0	25	2.3	2.4	0.17	0.5	—
2	0.10	2.5	35	3.0	—	0.11	0.5	—
2	0.10	2.5	50	4.5	—	0.11	0.5	—
10	1.0	0.0	25	27.0	28.0	*	0.66	0.96
11	0.10	0.0	25	3.2	3.6	*	0.64	1.6
12	0.05	0.0	25	1.6	1.7	*	0.66	1.9
13	0.01	0.0	25	0.23	0.29	*	0.65	2.3

* In this case a migration current was present, since there was no supporting electrolyte present; therefore the values obtained for b are difficult to interpret.

Except for the very dilute solutions of iron(III)-sulfate the currents i_0 and i_a are relatively small compared to the limiting current density, I_d; nevertheless corrections were made, as previously indicated and i_c was calculated. Various "real" polarization curves (E versus i_c) are shown in Fig. 5. In general, the curves are very similar to those obtained with platinum, except that in the case of aluminum the whole curve is shifted to more anodic potentials by about 0.75 v. The limiting diffusion current densities for the reduction of iron(III)-sulfate obtained with aluminum were about the same as those obtained with platinum. Some values are shown in Table II.

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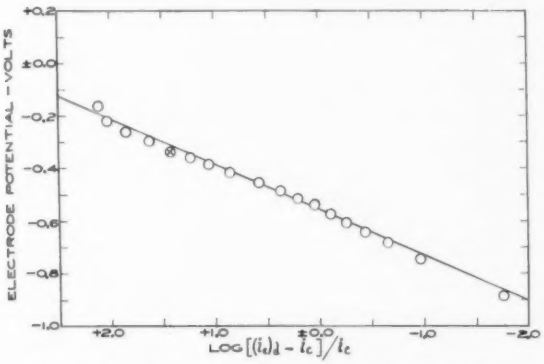

FIG. 6. The "real" polarization curve for the reduction of iron(III)-sulfate on aluminum at 25.0°C. ⊗-designates the open circuit values.

A typical result is shown in Fig. 6.

Although the values of b are about the same as for cerium sulfate the $E_{\frac{1}{2}}$ is about 0.25 v more anodic. Various values are given in Table II. The values of $E_{\frac{1}{2}}$ were generally reproducible to ±0.05 v; in a few cases variations of about ±0.1 v did occur.

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The experimental results indicate that the reaction of aluminum with iron sulfate may be interpreted by the theory of the "mixed potential" which, in this case, postulates two separate reactions governed by a common electrode potential. These are the cathodic reaction, which involves the reduction of iron(III)-sulfate, and the anodic reaction,

Evolution of gas was never observed on the surface of aluminum while on open circuit.

TABLE I. *Composition of Solutions*

Solutions	$Fe_2(SO_4)_3$ moles/l	$FeSO_4$ moles/l	H_2SO_4 moles/l	pH
1	0.01	0.0	2.5	—
2	0.10	0.0	2.5	—
3	0.20	0.0	2.5	—
4	0.30	0.0	2.5	—
5	0.50	0.0	2.5	—
6	0.0	0.50	2.5	—
7	0.10	0.0	0.50	—
8	0.10	0.0	4.0	—
9	0.10	0.0	5.0	—
10	1.0	0.0	0.0	0.96
11	0.10	0.0	0.0	1.6
12	0.05	0.0	0.0	1.9
13	0.01	0.0	0.0	2.3

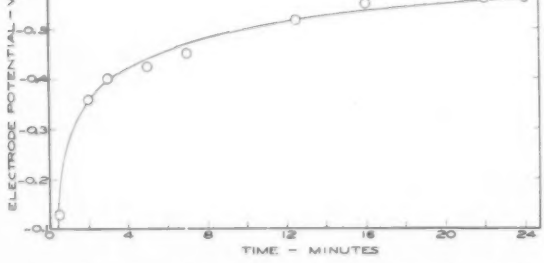

FIG. 1. Time-potential relationship in iron sulfate solution 1 at 25.0°C.

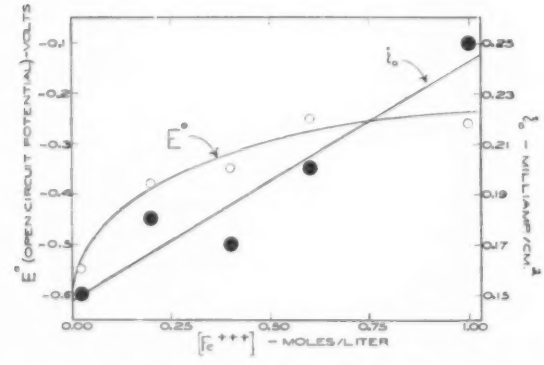

FIG. 2. Electrode potential and local action current on open circuit as a function of the iron(III)-sulfate concentration in solutions 2.5*M* in H_2SO_4.

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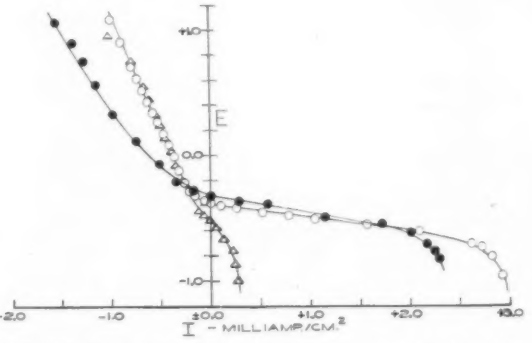

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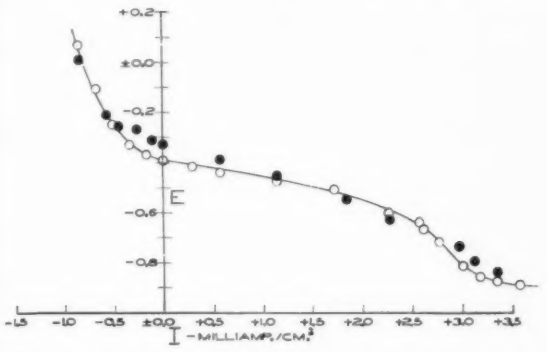

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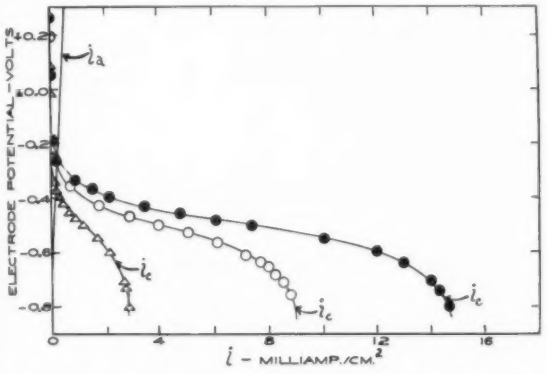

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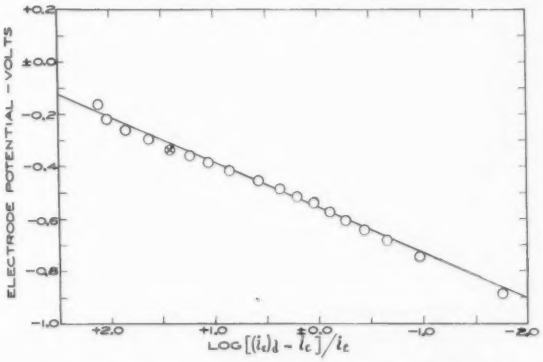

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which consists of the dissolution of aluminum. These two reactions are governed by the electrical potential difference which exists between the aluminum and the solution.

Since the thermodynamically reversible oxidation potential of aluminum in acid solutions is -1.9 v, while that of iron(III)-sulfate is about $+0.50$ v (2), it is evident that both reactions show a large polarization effect. The data, therefore, indicate that the dissolution of the aluminum is under both anodic and cathodic control.

Although the reduction of iron(III)-sulfate is highly irreversible, it yields a rather well-defined polarization curve and limiting current density. The latter is equal to that obtained on an inert metal such as platinum. The anodic polarization curve (E versus i_a) is linear within the potential ranges reported and is primarily a function of temperature and acid strength.

As suggested before (1), a possible explanation for the electrode behavior of aluminum is that the metal is covered by a very thin, compact, and continuous film of amorphous oxide. The "hysteresis" effect reported above might be accounted for on this basis. Thus, when the aluminum is cathodically polarized from the open circuit potential to more anodic potentials (up to the top of the cathodic polarization curve) there is a tendency for the film to become thinner. On coming back down the curve the reaction is then taking place on a thinner film and since the thinner the film, the more cathodic the required potential for any given i_c, the curve is displaced to more noble values. Obviously, this explanation can only be regarded as tentative at the present time.

Any discussion of this paper will appear in a Discussion Section, to be published in the December 1951 issue of the JOURNAL.

REFERENCES

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2. W. M. LATIMER, "Oxidation Potentials," Prentice Hall, Inc., New York (1935).

The Kinetics of Oxidation-Reduction Electrode Reactions[1]

J. V. Petrocelli

The Patent Button Company, Waterbury, Connecticut

ABSTRACT

A discussion of the kinetics of oxidation-reduction electrode reactions is presented. It is shown that the electrode reactions may be treated as rate processes and a general expression for the electrode potential-current density relationship is derived. This equation shows how the polarization curves may behave under conditions where concentration overvoltage and activation overvoltage are involved. It is suggested that the use of this equation may allow such important factors as "exchange current" and "transfer coefficients" to be evaluated and thus contribute to our knowledge of electrode reaction mechanisms.

Introduction

Although a great many studies have been made on the subject of overvoltage and several theories have been advanced to describe the phenomena, there is, as yet, no general agreement on the rate determining process (1–3). In the case of hydrogen overvoltage, where most all of the experimental work has been done, the theories may be divided into two groups. According to one group the rate determining process is the discharge of the ion, while according to the other it is the combination of the discharged atoms on the electrode surface. An excellent review of these theories is given by Bockris (3).

Comparatively little work has been done on other oxidation-reduction electrodes. In many cases the overvoltage at these electrodes is considered as due entirely to concentration polarization and they are often referred to as "reversible electrodes." The only significant theory concerning their mechanism is that advanced by Butler, which is based on the concepts of the thermionic work function of the metal and the electron energy levels of the ions in solution (4).

More detailed investigations of oxidation-reduction electrode systems should be of considerable value, not only for their own intrinsic value, but for the knowledge they may contribute to the general subject of overvoltage and the mechanism of electrode reactions. We have, for example, the following rather important question still unanswered. If the slow step in the reduction of hydrogen ions is bound up with the discharge of the ion, as in Gurney and Fowler's theory (5), why aren't appreciable overvoltages encountered with all oxidation-reduction electrodes?

[1] Manuscript received September 18, 1950. This paper prepared for delivery before the Washington Meeting, April 8 to 12, 1951.

In the case of hydrogen overvoltage where the following relationship applies between the current density and the electrode potential

$$i = i_0 \exp [\alpha V\mathbf{F}/RT]$$

a great deal of emphasis has been placed on the "constant" α and its interpretation and relatively little on the constant "i_0." There is reason to believe that α may have the same value for most electrode systems while i_0 may be very much a characteristic of the oxidation-reduction system and the electrode surface.

The present work is an attempt to derive a general expression for the current-electrode potential relationship for oxidation-reduction electrodes, which contains constants corresponding to those of the hydrogen system, with the hope that it will contribute to a better understanding of the mechanism of electrode reactions and overvoltage.

Electrode Reactions as Rate Processes

When an inert metal such as platinum is immersed in a solution containing an oxidation-reduction system, electron transitions take place from the metal to the oxidized component of the system and from the reduced component to the metal. We shall designate the former as the forward or cathodic reaction and the latter as the backward or anodic reaction. When equilibrium is finally achieved there is an electrical potential difference established between the metal and the solution and the rates of the forward and backward reactions become equal.

Under the equilibrium conditions there is no net flow of current; if the electrode potential is changed from this equilibrium value by means of an external circuit, the rate of one of the above reactions increases relative to the other. The difference in the rates of the two reactions will be given by the external current and the magnitude of this external

current will depend upon the change introduced in the electrode potential. These electrochemical reactions which take place at the electrode may be considered as rate processes.

Let v_1 equal the velocity of the cathodic or forward reaction:

$$A^{a+} + ne^- \rightarrow A^{(a-n)+}$$

and v_2 the velocity of the anodic or backward reaction:

$$A^{(a-n)+} \rightarrow A^{a+} + ne^-.$$

These velocities may then be expressed in terms of current density as follows:

$$i_c = n\mathbf{F}v_1$$

and

$$i_a = n\mathbf{F}v_2 .$$

On open circuit when the system is at equilibrium, the electrode potential may be designated as V^0 and we have,

$$i_c = i_a = i_0$$

where i_0 may be designated the "exchange current density." It should be noted that V^0 as defined here depends upon the particular cell under investigation and is not the thermodynamically defined standard potential for the system.

When the electrode is polarized by means of an external current density, I, the following relation will be true:

$$I = i_c - i_a \qquad \text{(I)}$$

where a positive value of I signifies cathodic polarization and a negative value anodic polarization. For any current I to flow the electrode potential must change from the equilibrium value V^0. If we designate this change by ψ, where $\psi = V - V^0$, we may define ψ as the overvoltage where negative values of ψ designate cathodic polarization, and positive values anodic polarization. Here V is the electrode potential when the current I is flowing.

It should be noted that no actual over-all reaction or current I is possible without ψ having some finite value. This is embodied in the fundamental concept that no net reaction is possible in an absolutely thermodynamically reversible process. In general, however, some systems may undergo change under conditions which approach the reversible ones very closely. In the case under discussion it will be seen that the smaller I is relative to i_0, the closer will the reaction proceed to thermodynamically reversible conditions.

If it is assumed that the electrode reactions require an activation energy, as is the case with many physicochemical reactions, we may develop the following relationships without assuming any particular mechanism (6).

We may write:

$$i_c = k_1C_1 \exp [-\alpha Vn\mathbf{F}/RT] \qquad \text{(II)}$$

$$i_a = k_2C_2 \exp [\beta Vn\mathbf{F}/RT] \qquad \text{(III)}$$

where k_1 and k_2 are the rate constants for the cathodic and anodic reactions, expressed in terms of current density, respectively; C_1 and C_2 the concentrations of the reacting ions (strictly speaking the activities) at the immediate surface of the electrode, V is the electrode potential, α is the portion of the electrical potential difference across the energy barrier which acts in the cathodic direction, while β is the portion acting in the anodic direction. $\mathbf{F}$, R, n, and T have their usual meanings.

There is some evidence that hydrogen overvoltage may be independent of the hydrogen ion concentration. If this is the case equations (II) and (III) would need to be modified for this reaction. Frumkin (7) has made an attempt to avoid this difficulty by taking into account the difference in the hydrogen ion concentration in the bulk of the solution and in the electrical double layer. Since the experimental evidence (8) on this point does not seem to be conclusive no further details will be attempted here.

It should be pointed out that in some cases, at least, α and β may be dependent on the electrode potential.

At equilibrium, on open circuit, $I = 0$, $V = V^0$ and

$$i_0 = k_1C_1^0 \exp [-\alpha V^0n\mathbf{F}/RT] = k_2C_2^0 \exp [\beta V^0n\mathbf{F}/RT] \qquad \text{(IV)}$$

where C^0 is the concentration of the reacting ion in the bulk of the solution. It should be noticed that this equation is equivalent to the expression for the equilibrium electrode potential obtained from thermodynamics, as it should be, namely:

$$V^0 = \frac{2.3RT}{(\alpha + \beta)n\mathbf{F}} \log C_1^0/C_2^0 + \text{Const.} \qquad \text{(V)}$$

Using equations (I), (II), and (III), we arrive at the following relationship for the electrode when it is polarized:

$$I = k_1C_1 \exp [-\alpha V^0n\mathbf{F}/RT] \exp [-\alpha\psi n\mathbf{F}/RT] - k_2C_2 \exp [\beta V^0n\mathbf{F}/RT] \exp [\beta\psi n\mathbf{F}/RT]. \qquad \text{(VI)}$$

And making use of equation (IV) we have:

$$I = i_0\{C_1/C_1^0 \exp [-\alpha\psi n\mathbf{F}/RT] - C_2/C_2^0 \exp [\beta\psi n\mathbf{F}/RT]\}. \qquad \text{(VII)}$$

If we assume that there is a sufficient amount of an indifferent electrolyte present so that the migration current of the ions reacting at the electrode is negligible, the actual concentrations C_1 and C_2 at the electrode surface at any given external current density I will be governed by Fick's law of diffusion (9). If it is further assumed that linear diffusion is involved we have:

$$I = n\mathbf{F}D_1/l[C_1^0 - C_1] \qquad \text{(VIII}a\text{)}$$

$$I = n\mathbf{F}D_2/l[C_2 - C_2^0] \qquad \text{(VIII}b\text{)}$$

where D is the diffusion coefficient of the ion in question and l the thickness of the diffusion layer. When an electrode is polarized so that an external current I flows, both relations (VII) and (VIII) must be simultaneously satisfied.

Using equations (VIII) the concentration of a reacting ion may be expressed in terms of the external current density I as follows:

When the value of C_1 approaches zero the cathodic current density I approaches the limiting value

$$(I_c)_d = n\mathbf{F}D_1/l \cdot C_1^0. \qquad \text{(IX}a\text{)}$$

Similarly, when C_2 approaches zero the anodic current density, I, approaches the limiting value

$$(I_a)_d = [I_{C_2=0}] = n\mathbf{F}D_2/l \cdot C_2^0. \qquad \text{(IX}b\text{)}$$

For convenience we shall omit the subscript d, with the understanding that I_c and I_a are the absolute values of the limiting diffusion current densities for the cathodic and the anodic reactions, respectively.

Upon dividing corresponding sides of equations (VIIIa) and (IXa), and of equations (VIIIb) and (IXb), respectively, and regrouping, it follows that

$$\frac{C_1}{C_1^0} = \frac{I_c - I}{I_c} \qquad \text{(IX}c\text{)}$$

and

$$\frac{C_2}{C_2^0} = \frac{I_a + I}{I_a}. \qquad \text{(IX}d\text{)}$$

Substituting equations (IXc) and (IXd) in equation (VII) yields

$$I = i_0\left\{\frac{I_c - I}{I_c}\exp[-\alpha\psi n\mathbf{F}/RT] - \frac{I_a + I}{I_a}\exp[\beta\psi n\mathbf{F}/RT]\right\}. \qquad \text{(X)}$$

This equation may be put into a logarithmic form yielding:

$$\psi = \frac{2.3RT}{(\alpha + \beta)n\mathbf{F}}\log\left\{\frac{I_c - I}{I_a + I} - \frac{I}{i_0/I_c[I_a + I]\exp[-\alpha\psi n\mathbf{F}/RT]}\right\} + \frac{2.3RT}{(\alpha + \beta)n\mathbf{F}}\log I_a/I_c. \qquad \text{(XI)}$$

Letting

$$f_c \equiv \frac{I_c - I}{I_c}$$

$$f_a \equiv \frac{I_a + I}{I_a} \qquad \text{(XII)}$$

and

$$A \equiv f_c\exp[-\alpha\psi n\mathbf{F}/RT]$$

$$B \equiv f_a\exp[\beta\psi n\mathbf{F}/RT] \qquad \text{(XIII)}$$

we may write equation (X) as follows:

$$I = i_0[A - B]. \qquad \text{(XIV)}$$

Concentration Overvoltage

It is clear that when the electrode is polarized and a current I flows, the concentration of the reactants in the vicinity of the electrode will change. In our case the factors f_c and f_a account for these changes. If i_0, the exchange current, is large compared to I, it will be seen that equations (X) and (XI) approach the following form:

$$\psi_c = \frac{2.3RT}{(\alpha + \beta)n\mathbf{F}}\left\{\log\frac{I_c - I}{I_a + I} + \log\frac{I_a}{I_c}\right\} \qquad \text{(XV)}$$

which is the usual expression derived for a so-called reversible electrode. Followng Agar and Bowden (9) we will designate the overvoltage in this case as "concentration overvoltage," and designate it as ψ_c. Under such conditions the electrode reaction is proceeding very closely to equilibrium conditions and the overvoltage is due almost entirely to the concentration changes. The electrode potential as a function of current density is diffusion controlled. Experimentally, a plot of ψ versus $\log (I_c - I)/(I_a + I)$ yields a straight line with a slope equal to $2.3RT/(\alpha + \beta)n\mathbf{F}$. Generally, systems will show this behavior if $i_0 \gg I_c$ and $i_0 \gg I_a$ as well.

Activation Overvoltage

If for given diffusion conditions i_0 is of the same order of magnitude or much less than I_c and I_a owing to a relatively high activation energy of the surface reaction, the overvoltage for a given value of I will have a greater magnitude than if it were due to concentration changes only. In such cases it may be said that activation control prevails and generally this will be the case when $i_0 \ll I_c$ and $I < I_c$ for cathodic polarization and $i_0 \ll I_a$ and $I < I_a$ for anodic polarization. Equations (X) and (XI)

will then have to be used in their present form. If we designate that part of the overvoltage which lowers the activation energy of a surface reaction as ψ_{ac}, we may write $\psi = \psi_{ac} + \psi_c$ indicating the superposition of the two effects both of which are included in equations (X) and (XI).

In the extreme case, where $i_0 \ll I_d$, one of the terms on the right side of equation (X) will drop out as ψ increases. The term which becomes negligible will depend upon whether the electrode is cathodically or anodically polarized. Thus for cathodic polarization we will have

$$I = i_0 f_c \exp [-\alpha\psi n\mathbf{F}/RT].$$

For the general case if we substitute $\psi = \psi_{ac} + \psi_c$ into equation (X), and at the same time keep in mind that

$$\exp\left[\frac{(\alpha + \beta)\psi_c n\mathbf{F}}{RT}\right] = f_c/f_a \qquad \text{(XVI)}$$

we will obtain the following expression:

$$\exp [-\alpha\psi_{ac} n\mathbf{F}/RT] - \exp [\beta\psi_{ac} n\mathbf{F}/RT = \frac{I}{i_0 f_c \exp [-\alpha\psi_c n\mathbf{F}/RT]} \qquad \text{(XVII)}$$

which by using equation (XVI) gives the following expression for the activation overvoltage:

$$\psi_{ac} = \frac{2.3RT}{(\alpha + \beta)n\mathbf{F}} \log \{1 - I/i_0 A\}. \qquad \text{(XVIII)}$$

In the special case that $\alpha = \beta$ equation (XVII) may be written as follows:

$$\sinh (\alpha\psi_{ac} n\mathbf{F}/RT) = -\tfrac{1}{2} \frac{I}{i_0 f_c \exp [-\alpha\psi_c n\mathbf{F}/RT]} \qquad \text{(XIX)}$$

which for small values of ψ_{ac} or when $\alpha\psi_{ac} n\mathbf{F}/RT < 1.0$, becomes

$$\psi_{ac} \cong -\frac{RT}{2\alpha n\mathbf{F} i_0 f_c \exp[-\alpha\psi_c n\mathbf{F}/RT]} \cdot I. \qquad \text{(XX)}$$

For a small range of current densities the product $f_c \exp [-\alpha\psi_c n\mathbf{F}/RT]$ is practically constant so that in this range ψ_{ac} varies linearly with I.

Ohmic Resistances

In case that an ohmic resistance, r, is present so that the ohmic potential difference, E_r, developed when current flows, is included in the electrode potential, the total overvoltage as measured will contain the term:

$$E_r = Ir. \qquad \text{(XXI)}$$

This may occur when the solution near the electrode has a very low conductivity, or if a poorly conducting film is present on the surface of the electrode. In the latter case the IR term may be called a resistance overvoltage (9).

A rather important case might arise where the electrode reaction does not involve an activation overvoltage but for one reason or another does involve an ohmic potential difference in addition to concentration polarization. In this case, if we let $I_c = I_a$ for simplicity, we have:

$$\psi_m = \psi_c + E_r = \frac{2.3RT}{(\alpha + \beta)n\mathbf{F}} \log \frac{I_c - I}{I_a + I} + Ir \qquad \text{(XXII)}$$

where ψ_m is the measured overvoltage. The slope of the log curve may be obtained by differentiating equation (XXII) which gives

$$\frac{d\psi_m}{d \log \dfrac{I_c - I}{I_a + I}} = \frac{2.3RT}{(\alpha + \beta)n\mathbf{F}} + 2.3r \left\{\frac{(I_c - I)(I_a + I)}{I_c + I_a}\right\}. \qquad \text{(XXIII)}$$

Now, although the slope is a function of the current, within the current ranges realizable in the laboratory, the slope may be "approximately constant." Thus, experimentally obtained slopes of the log curve which are greater than $2.3RT/(\alpha+\beta)n\mathbf{F}$ may be due to an ohmic resistance.

It is important to note that within certain current-potential regions a linear relation between a "measured" overvoltage and current might be due to either an activation overvoltage or an ohmic overpotential as shown by equations (XX) and (XXI).

Absolute Reaction Rates

If we wish to use the concepts of the theory of absolute reaction rates (6) our equations (II) and (III) may be written as follows:

$$i_c = \frac{n\mathbf{F}}{N}\left[\frac{kT}{h}\right] C_1 \exp (-\overline{\Delta F_1^*}/RT) \cdot \exp (-\alpha\psi n\mathbf{F}/RT)$$
$$i_a = \frac{n\mathbf{F}}{N}\left[\frac{kT}{h}\right] C_2 \exp (-\overline{\Delta F_2^*}/RT) \cdot \exp (\beta\psi n\mathbf{F}/RT) \qquad \text{(XXIV)}$$

where

$$\overline{\Delta F_1}^* = \Delta F_1^* + \alpha n\mathbf{F}V^0$$
$$\overline{\Delta F_2}^* = \Delta F_2^* + \beta n\mathbf{F}V^0 \qquad \text{(XXV)}$$

and ΔF^* is the standard free energy of the activation processes when the electrical potential difference at the electrode interface is equal to zero.

Accordingly, we may express the exchange current as

$$i_0 = \frac{n\mathbf{F}}{N}\left[\frac{kT}{h}\right] C^0 \exp (-\overline{\Delta F^*}/RT) \qquad \text{(XXVI)}$$

Discussion

As already noted the actual current-potential relationship for any oxidation-reduction electrode system will depend very much upon the value of i_0/I_d. For certain values of this ratio where an activation overvoltage is involved a linear relation may still be found between ψ and the log $(I_c - I)/(I_a + I)$ even though the true relation is given by equation (XI), but the slope will be greater than $2.3RT/(\alpha+\beta)n\mathbf{F}$, the value for the so-called reversible electrode. The actual value of the slope will depend upon the value of i_0/I_d. The greater this ratio the closer will the slope approach the reversible value. In case that $\alpha \neq \beta$, more than one slope may be obtained.

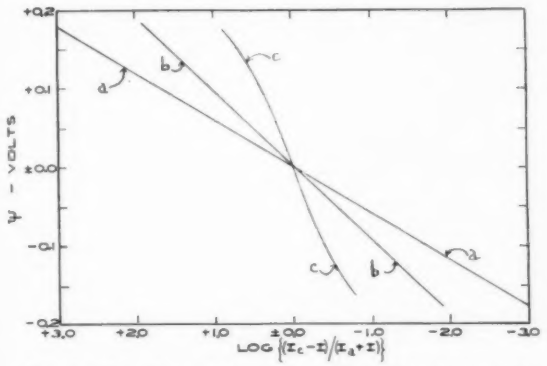

FIG. 1. The effect of the ratio i_0/I_d on the slope of the log curve. $\alpha = \beta = 0.5$, $I_a = I_c = 5.0$ ma/cm². Curve a—$i_0/I_d = 200$; curve b—$i_0/I_d = 1.0$; curve c—$i_0/I_d = 0.10$.

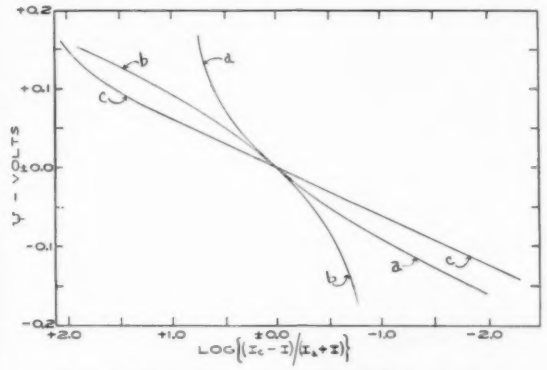

FIG. 2. Effect of i_0/I_d, α and β on the log curve
Curve a—$i_0 = 2.5$ ma/cm², $\alpha = 0.75$, $\beta = 0.25$
Curve b—$i_0 = 2.5$ ma/cm², $\alpha = 0.25$, $\beta = 0.75$
Curve c—$i_0 = 100$ ma/cm², $\alpha = 0.75$, $\beta = 0.25$
In all cases $I_c = I_a = 5.0$ ma/cm².

Keeping in mind that the experimental values of the limiting current density realizable in the laboratory are of the order of magnitude of ma/cm² various values of ψ have been calculated for given values of i_0, I_d, α, β, etc., using equation(X). Using the data so obtained, various plots of ψ versus log $(I_c - I)/(I_a+I)$ have been made. Typical results are given in Table I and shown in Fig. 1, 2, and 3.

The values given in the table and the curves of Fig. 1 show the effect of varying the ratio i_0/I_d. It will be seen that, even though an activation overvoltage is involved, linear log plots may be obtained, and that the slope increases as i_0/I_d decreases. The curves of Fig. 2 and 3 show the effect of α, β, and I_c/I_a on the log plot. When $\alpha \neq \beta$ there is a tendency for the log plot to have two linear sections whose slopes depend upon the values of α and β. This tendency diminishes as the ratio i_0/I_d increases. It should also be noticed that the ratio I_c/I_a will influence the slope of the curves.

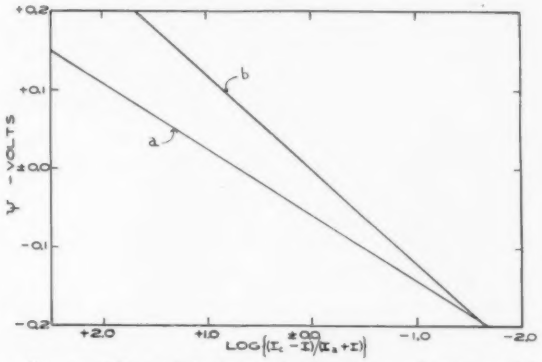

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TABLE I. *The effect of i_0/I_d on the slope of ψ versus log $\frac{I_c - I}{I_a + I}$ when $I_c = I_a = 5.0$ ma/cm².*

i_0 ma/cm²	i_0/I_d	Slope at 25°C
10^4	2000	0.059
10^3	200	0.059
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5	1	0.095
2.5	0.5	0.12
0.5	0.1	0.27
0.05	0.01	2.1

A very interesting and important case is when either α or β is equal to zero. In this case our equation (X) becomes very similar to the one arrived at by Butler (4) and previously mentioned. In such a case, say $\beta = 0$, if i_0 is less than the anodic limiting current density which the ion in question is able to support in accordance with Fick's diffusion law, equation (IX), it will not be possible to experimentally obtain this anodic limiting current density which is predicated by diffusion theory when the electrode is submitted to anodic polarization. This

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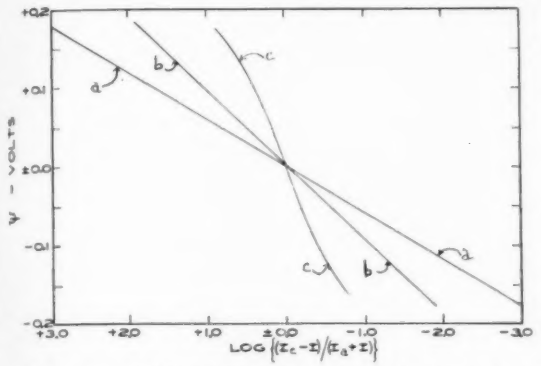

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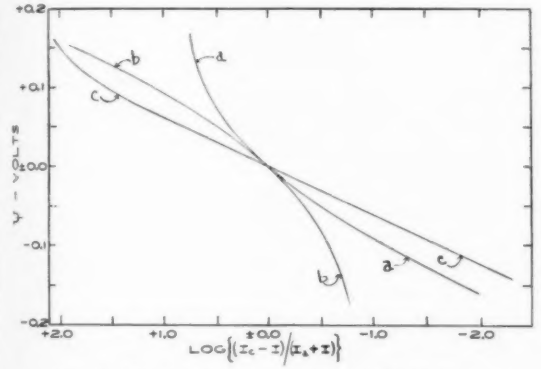

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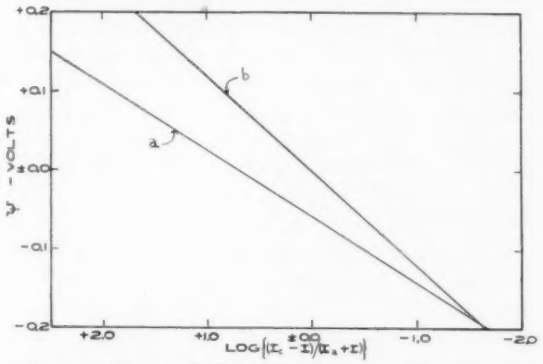

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is readily apparent when it is realized that in such a case the overvoltage cannot effect the anodic current density i_a, e.g., our equation (X) becomes

$$I = i_0 f_c \exp(-\alpha\psi n\mathbf{F}/RT) - i_0 f_a . \quad \text{(XXVII)}$$

The same would be true for the cathodic limiting current density predicated by diffusion theory if α were zero.

From an experimental point of view it may be anticipated that a direct test of equation (X) may be difficult for electrode reactions which only involve concentration overvoltage, large value of i_0/I_d. In such cases one is concerned with a small difference between two large terms which always introduces rather large uncertainties; in addition, the factors f_c and f_a are dominant and it may be difficult to control experimental conditions so that the linear law of diffusion is strictly operative. On the other hand the equation should be useful to obtain at least approximate values, if not exact ones, of i_0, α, and β for reactions which do involve an activation overvoltage.

In the case of reactions where i_0/I_d is not very large it may be possible to decrease this ratio by increasing I_d with stirring. In this way a reaction which is predominantly under diffusion control may be converted to one which is under activation control.

Since the completion of this work, our attention has been called to some recent work by Vetter (10) and Gerischinger (11) which is also concerned with the theoretical expression of i_0 and its measurement.

Any discussion of this paper will appear in a Discussion Section, to be published in the December 1951 issue of the JOURNAL.

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Cathode Polarization Potential during Electrodeposition of Copper

I. Nonreproducibility in Acid Copper Sulfate Solutions[1]

L. L. Shreir

Battersea Polytechnic, London, England

AND

J. W. Smith

Bedford College for Women, London, England

ABSTRACT

The constant state polarization potential (C.S.P.) of the cathode during the electrodeposition of copper from copper sulfate-sulfuric acid solutions depends upon the conditions of preparation and storage of the solution and the time which it is kept after preparation. Freshly prepared solutions usually give fine deposits, associated with high C.S.P. values, but on keeping there is a decrease of C.S.P. value, accompanied by a coarsening of the crystal structure. The C.S.P. value is raised again, and a fine structure deposit obtained, after the solution has been treated with oxidizing agents or submitted to prolonged electrolysis. Evidence has been obtained that this effect is due to the presence in the reagents, or to formation during storage of the solution, of a very slight trace of impurity which has the unusual property of reducing the C.S.P. value and increasing the crystal size in the deposit. The formation of this impurity is associated with traces of contamination in ordinary distilled water, and a method for the preparation of solutions which remain stable for several months has been developed.

Introduction

Although the cathode polarization potential during the electrodeposition of copper from copper sulfate-sulfuric acid solutions has been studied by several workers (1–4) there has been little accord between the results obtained. This is doubtlessly due in part to the different techniques used in the measurements and to the influence of the structure of the copper base upon the electrodeposit, but another important factor has been the variable period of electrolysis allowed to elapse before the measurements were taken.

The variation of the cathode polarization potential with time was studied in detail by Gauvin and Winkler (5), who used rigidly controlled experimental conditions in an attempt to obtain a definite and reproducible value. Their copper block cathodes were prepared by grinding with successively finer grades of emery paper, finishing with 000 grade, to produce smooth plane surfaces, and then by degreasing and etching in a sulfuric acid-nitric acid mixture before mounting in the improved form of Haring cell used for the measurements. With an electrolyte containing 125 g/l $CuSO_4 \cdot 5H_2O$ and 50 g/l H_2SO_4, and maintaining a constant apparent current density of 2.0 amp/dm^2 at 24.8°C, polarization readings were taken at intervals after establishing the polarizing current. The readings taken immediately or, say, five minutes after applying the current were erratic; after 10 minutes there was usually a slight increase in the polarization, followed by a decrease, until after about 20 minutes the potential became constant at 75–80 mv (Fig. 1, curve *A*). This steady value was termed the "constant state polarization"; it was apparently independent of the initial polarization potential and thus represented a constant value which could be reproduced under the specified experimental conditions. Gauvin and Winkler (6) suggested that the change of the polarization potential with time was due, not to the slow attainment of steady state conditions in the cathode layer, as this would probably be established in about two minutes, but to the increase of the true surface area of the cathode produced by the electrodeposition and the consequent reduction in the true current density. The irregularity of the values observed immediately after closing the circuit was, therefore, attributed to the inability to reproduce accurately, by polishing, the same surface characteristics for each cathode base.

This view was supported by the polarization-time

[1] Manuscript received May 5, 1950. This paper prepared for delivery before the Buffalo Meeting, October 11 to 13, 1950.

curves they obtained for deposition on bases of varying crystal sizes prepared by the electrodeposition of copper at different current densities. There was a gradual increase in the polarization potential with time when the base structure was finer than the deposit, and a gradual decrease when the base was coarser than the deposit. These results were at variance with the theory of Blum and Rawdon (7), which predicted that a change from a coarsely crystalline to a fine deposit should be associated with an increase in polarization.

From these observations Gauvin and Winkler inferred that the lack of accord between the results reported by other workers was due to the custom of measuring the polarization potential at a given current density after an arbitrary time, say five minutes, instead of allowing the steady state to be established.

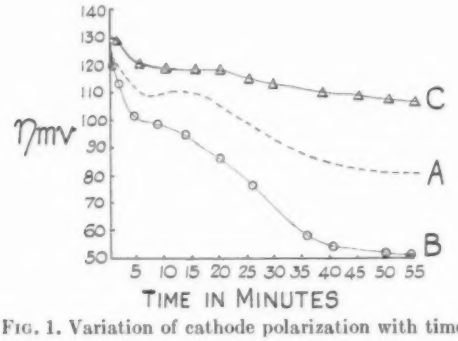


FIG. 1. Variation of cathode polarization with time

Preliminary Investigation

The technique established by Gauvin and Winkler suggested a convenient means of studying the effect of complex ion formation on the cathode polarization potential of copper. As a preliminary to such studies, therefore, the measurements of these authors were repeated, using a Haring cell of the form described by them. Although their procedure was followed in every particular, the early results were erratic. With a solution containing 125 g/l $CuSO_4 \cdot 5H_2O$ and 50 g/l H_2SO_4 (the "standard" electrolyte) and an apparent current density of 2.0 amp/dm^2 the constant state polarization (C.S.P.) values at 25.0°C ranged from 50 to 60 mv (Fig. 1, curve *B*), although sometimes values outside this range were obtained. The deposits generally conformed to the description given by Gauvin and Winkler, being "coarsely crystalline" (Fig. 2, No. 1), but sometimes the deposits were not uniform and comprised an upper coarsely crystalline area and a lower area of fine deposit (Fig. 2, No. 2, 3, and 4), the lower C.S.P. values being associated with the deposits which had the larger areas of coarse deposit.

Attempts to ascertain the causes of the irregularities and the inability to reproduce Gauvin and Winkler's results had little success, but, during a period of cold weather, there was a change in the results obtained, although the temperature was still kept at 25° C during electrolysis. The deposits formed under the standard conditions were now finely crystalline (Fig. 2, No. 5) resembling the lower areas of the heterogeneous deposits obtained previously. The polarization potential changed only slightly with time (Fig. 1, curve *C*), and the C.S.P. value was about 110 mv. The results obtained in repeat runs on fresh batches of solution were closely concordant, and the change in the character of the deposit showed that the different polarization values were not due to errors in the measurement technique.

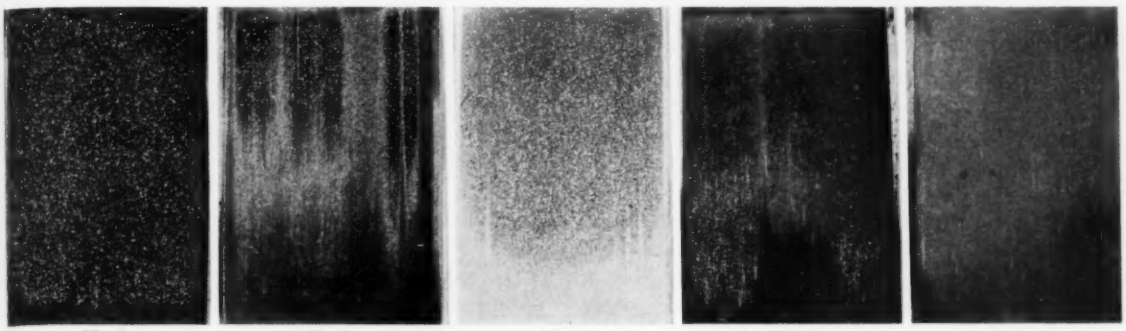
These preliminary studies indicated, therefore, that even under rigidly controlled experimental conditions, and with the effect of the base structure eliminated by studying the C.S.P. value, reproducible polarization values were not so easy to obtain as had previously been supposed. Before any investigation of the effect of complex ion formation on the cathode polarization potential could be usefully prosecuted, therefore, it was essential to investigate fully the factors involved in the determination of the C.S.P. values, in order to find the cause of the widely divergent behavior observed under conditions which were apparently identical.

Apparatus and Methods

The total cathode polarization potential (η) can be regarded as the sum of two factors: η_a the activation polarization, and η_c the concentration polarization. A third term, η_r, the potential drop due to the resistance in the stable diffusion layer, is sometimes included but this is difficult to determine separately and any such effect has been included in η_a. As η_c is determined by diffusion and convection, and hence is affected by such factors as the area of the cathode and the shape of the containing vessel, the results of measurements of η are dependent upon the method used. Hence when comparing C.S.P. values under rigidly controlled conditions it was desirable to compare the results obtained when the measurements were made in the same vessel and with identical electrodes by the two established methods, viz., the Haring cell method and the procedure involving the use of a separate reference electrode in conjunction with a Luggin capillary.

The Haring cell has the advantage that it gives an average result for the whole cathode area, whereas the half-cell and capillary yield a value representing only the small area in contact with the capillary tip. The heterogeneous deposits obtained in the preliminary work therefore favored the use of the Haring cell, as even when the capillary was placed away

from the cathode during measurement, different results were obtained according to whether the capillary tip was brought into contact with a coarse or a fine area of the cathode surface in determining the resistance correction. This advantage did not apply in later work when the conditions for obtaining uniform deposits had been ascertained. However the use of the Haring cell eliminates the liquid junction potential inherent in the half-cell method, and has been employed in this work for most of the measurements of η. For the separate determination of η_a it



No 1 No. 2 No. 3 No. 4 No. 5

FIG. 2. Photographs of deposits

was necessary to use stirred solutions. Under these conditions the Haring cell was found to be impracticable, leaving no alternative but to use a half-cell and Luggin capillary.

Haring cell.—In the usual forms of Haring cell it is difficult to fit the cathode so that an exactly known surface area is presented to the electrolyte. Also, the production of a smooth cathode surface by grinding a copper block is time-consuming, and such drastic scouring of the surface may have a pronounced effect on the crystal development in the deposit caused by inclusions of small particles of emery (8).

The cell used in this work, designed to overcome these and other defects, was made of Perspex[2] 0.30 cm thick. In addition to being transparent, this material was found to be chemically resistant to the solutions used, and watertight joints were readily made by cementing with chloroform. A clamping arrangement permitted copper foil to be used as cathode. A piece of the foil slightly smaller than the end was placed on the flanged end of the cell (Fig. 3). This was covered with a rubber gasket and finally with a Tufnol[3] end-piece, the whole being secured with clamping screws. An adjustable Perspex stop, which could slide over the cathode face, prevented the foil from buckling owing to the pressure of the

[2] Polymerized methyl methacrylate.
[3] Laminated phenol formaldehyde resin.

screws. When unstirred solutions were used this was kept about 0.5 cm above the surface of the solution, but for experiments involving agitated solutions, where the level of the surface of the electrolyte was continuously changing, it was lowered so that exactly 10 cm^2 of the cathode surface was exposed to the solution. The gauzes and anode were located by slots cut in the sides of the cell.

This cell has the advantage that by adjusting the level of the solution to a mark on the side near the cathode a known and reproducible area of the cath

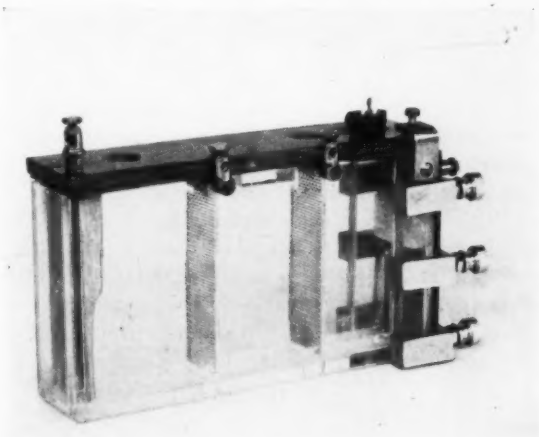


FIG. 3. Perspex Haring cell

ode is presented to the electrolyte. Further, the course of the deposition can be observed, and the deposits kept for future reference.

Calibration of the cell.—The Haring cell method is sound theoretically only if the gauzes are unpolarized and the interelectrode distances exactly equal. Attempts to determine the polarization potentials of the gauzes by means of a reference electrode were unsuccessful because of the unavoidable IR potential drop between the crimped surface of the gauze and the capillary tip. However, the gauzes were definitely

polarized to some extent owing to the concentration changes produced in the electrolyte during electrolysis, when the lower layers of the solution became richer in copper than the upper layers. This formed a concentration cell in which copper was dissolved from the upper portions of the gauzes and deposited on the lower portions, necessitating frequent renewal of the gauzes, particularly when measurements were made at high current densities.

Gauvin and Winkler (5) pointed out that it is impossible to position the gauzes so that the cell is divided into three compartments of exactly equal length, so it is essential to use a potentiometric method to correct for the inequalities. The method used in this work was a slight modification of that described by Gauvin and Winkler. The cell was charged with an unacidified solution containing 125 g/l of $CuSO_4 \cdot 5H_2O$, in which the anode and cathode polarizations did not exceed 12 mv for an apparent current density of 0.3–1.0 amp/dm². As the most consistent values were obtained when the potentials between the electrodes were as high as possible, a current density of 1 amp/dm² was used. All other

FIG. 4

conditions were similar to those existing during the polarization measurements, the area of cathode exposed to the electrolyte being 0.1 dm².

With the current leads connected to D and G (Fig. 4) the potential drops between D and F (x) and between E and F (y) were measured. The leads were then transferred to E and F and the potential drop (z) of this compartment at the same current density of 1 amp/dm² determined. Now

$$x = \eta_D + IR_A + IR_M + \eta_F \qquad \text{(I)}$$

and

$$z = \eta_E + IR_M + \eta_F \qquad \text{(II)}$$

where η_D, η_E, and η_F are the polarization potentials of the cathode D, which was made anodic, of the gauze E, and the gauze F, respectively, and IR_A and IR_M are the potential drops through the solution in compartments A and M respectively. Although η_D and η_E will differ, one applying to sheet copper and the other to gauze, both are small, and hence we have

$$x - z = IR_A.$$

Also, as the principle of the Haring cell is based upon the supposition that the gauzes remain unpolarized

$$y = IR_M .$$

By taking the lengths of these compartments as proportional to their IR potential drops a satisfactory correction was made for any inequalities of spacing. Concordant results were obtained when the current was passed through the cell in the reverse sense.

Preparation of the cathodes.—To insure a reproducible base surface, one roll of annealed copper foil 0.01 cm thick was used for all these investigations. The surface of the foil was far superior to that obtained by polishing with 000 grade emery paper, so that no scouring was necessary. The foil was first degreased in benzene and then cleaned electrolytically by making it the cathode in a hot solution containing sodium hydroxide (15 g/l), sodium carbonate (60 g/l), and sodium cyanide (7.5 g/l). It was then either acid etched or electrolytically polished, the former method being adopted in the earlier measurements so as to reproduce the conditions of Gauvin and Winkler. It was found that the most satisfactory electrolytic polishing (9) was obtained in a solution containing 635 ml/l of phosphoric acid. The cathode to anode areas were in the ratio 4:1, the cathode being supported 2.5 cm above the anode. Optimum brightness over the whole area (20 cm²) of the base was obtained with a current of 0.75 amp passed for about 20 minutes. After polishing, the specimen was removed from the bath, rinsed in water, and immersed in 10 per cent sulfuric acid to remove the white residue of copper phosphate. It was then washed again in water and mounted immediately in the cell.

Reference electrodes.—Although the calomel half-cell has been widely used for polarization measurements, it is evident that a mercurous sulfate electrode containing the same concentration of sulfuric acid as the electrolyte has an advantage in that the liquid junction potential is decreased. Both forms of electrode were used in these investigations, the same design of electrode vessel being employed in each case. This was a modification of Graham's electrode (10) but included a three-way tap in which the liquid junction was made, thereby avoiding contamination of the electrolysis bath with the solution from the half-cell. When the tap was turned so that all junctions in this tap were closed, the thin film of liquid around the ungreased stopper gave sufficient conductivity to permit readings to be taken.

Materials.—The sulfuric acid used was of AnalaR grade. AnalaR copper sulfate was twice recrystallized from distilled water before use. The water used in the earlier work was obtained from an ordinary laboratory still.

Measuring circuit.—The polarizing circuit comprised six 2-volt accumulators in series with three rheostats of 1000, 12, and 1 ohm resistance, respectively, to permit accurate adjustment of the current

over the range 0.02–0.40 amp. The current was measured with a calibrated Weston ammeter having shunts to give the ranges to 0.100, 0.200, and 0.500 amp, respectively, the scales being graduated in units of 0.001, 0.002, and 0.005 amp, respectively. The Tinsley potentiometer of range 0–1800 mv, graduated to 0.5 mv, could be modified to ranges of 180 and 18 mv, respectively. A Tinsley reflecting beam galvanometer of period 10 seconds, resistance 10 ohms, and deflection 14 mm per μa, was connected in series with a 10,000-ohm resistance. This resistance was kept in circuit during measurements with the Haring cell but short-circuited when using the reference electrode.

uated to contain sufficient solution to cover exactly 10 cm² of cathode surface (approximately 150 ml), was kept in a water thermostat maintained at 25.0° ± 0.05°C for 30 minutes before transfer to the cell which was mounted in the same thermostat. The cell was then leveled by the aid of a spirit level. Readings of the potential drops between the two gauzes F and E and between the gauze E and the cathode D were then taken at intervals.

TABLE I. *Variation of polarization potential with time in typical experiment at 2 amp/dm²*

Potentials in mv

Time (min)	Cell I				Cell II			
	C*	M‡	$\eta = C\text{-}M$	η (corrected)	C*	M‡	$\eta = C\text{-}M$	η (corrected)
0	668	553	115	108	690	580	110	113
2	673	552	121	114	690	581	109	112
5	670	552	118	111	688	581	107	110
12	666	550	116	109	685	581	104	107
21	665	550	115	108	684	579	105	108
33	664	551	113	106	683	580	103	106
45	662	552	110	103	682	580	102	105
50	662	552	110	103	681	580	101	104

* C = potential drop across cathode compartment, i.e., between D and E (Fig. 4).
‡ M = potential drop across middle compartment, i.e., between E and F.

Determination of correction factor

	Cell I			Cell II		
(*a*) *D as cathode, G as anode (see Fig. 4)*						
Potential difference between D and E with leads to D and G	1713	1712	1712	1755	1752	1750
Potential difference between E and F with leads to D and G ($= y$)	1670	1668	1670	1751	1747	1743
Potential difference between D and F with leads to D and G ($= x$)	3383	3380	3382	3506	3499	3493
Potential difference between E and F with leads to E and F ($= z$)	1691	1691	1691	1765	1762	1759
$x - z$	1692	1689	1691	1741	1737	1734
Average factor $(x - z)/y$	1691/1669 = 1.013			1737/1747 = 0.994		
(*b*) *G as cathode, D as anode*						
Average factor $(x - z)/y$	1.015			0.994		
Correction	−550 × 1.014 = −7 mv			580 × 0.994 = +3 mv		

Table I shows typical results obtained with two Haring cells in series, using the "standard" electrolyte at 2 amp/dm². The method of correction for inequalities in the cell distances is also illustrated.

Method of Operation with Haring Cell

Owing to the low thermal conductivity of the cells, the electrolyte, contained in a glass flask grad-

Method of Measurement with Mercury Reference Electrode

Two techniques are available for making polarization measurements with the half-cell: (*a*) the tip of

the capillary is pressed lightly but firmly against the surface of the cathode so as to eliminate as far as possible the *IR* drop of the solution, although a small *IR* drop must of necessity be present; and (*b*) the tip is placed away from the cathode and correction is made for the *IR* drop.

Method (*a*) has the disadvantage that the cathode surface in proximity to the capillary tip is screened from the electrolyte and it is frequently observed that the deposit at this point is coarser than over the remainder of the cathode. The results are therefore subject to error due to this effect. Method (*b*) eliminates this error but is limited to measurements at low current densities, as the correction for the *IR* drop depends on the current density. As it is unsatisfactory to make this correction by actual measurement of the distance between the capillary tip and the cathode surface, the following procedure was adopted. With the capillary about 1 cm from the cathode surface the potential was measured periodically until the C.S.P. value was attained. The tip was then moved to the cathode surface and the potential measured again, the *IR* drop due to the solution being thereby evaluated and the polarization figures corrected.

For the measurements of η_a, the Haring cell with the gauzes removed was found satisfactory. The stop was set so that an area of 2.5 x 4.0 cm was exposed, and the level of the electrolyte was kept about 1 cm above the lower edge of the stop. A constant cathode area was thus maintained in spite of the disturbance of the electrolyte surface through stirring. The fact that the rectangular shape of the cell was not so conducive to good circulation of the electrolyte as a cylindrical container was overcome by using a high speed stirrer placed about 1 cm from the cathode surface. Simultaneous measurements of η by the Haring cell method and of η_a by the reference electrode method could be carried out by using two cells connected in series.

Study of the Causes of the Irregularities

Effect of the Nature of the Surface of the Cathode Base

Since the modified Haring cell insured that reproducible cathode bases could be used, investigations were made to ascertain whether the abrupt change in the nature of the deposit observed in the preliminary studies could be attributed to variations in the pretreatment of the surface. The application of various methods of polishing, variation of the composition and temperature of the etching solution, and the use of anodic etching all had little effect. At this period of the investigation the coarse deposit and low C.S.P. value seemed to be unobtainable.

Effect of Storing the Electrolyte

Previous investigators has given no indication of rigid precautions in the preparation of the $CuSO_4$-H_2SO_4 electrolyte. In the preliminary measurements, the deposits were produced in each case in a thermostat at 25° C, but the mean temperature at which the solutions had been stored was higher for the solutions which gave the coarse deposit than for those which gave the fine deposit. Hence it seemed possible that the electrolyte was affected by standing to an extent which varied with the temperature.

Batches of the standard solution were therefore kept in glass-stoppered flasks at 30°C, C.S.P. determinations being made periodically with 150 ml samples which were discarded after use. With freshly-made solution the deposits were finely crystalline and the C.S.P. value was about 100 mv, but after keeping for 2–3 days the solution yielded a deposit

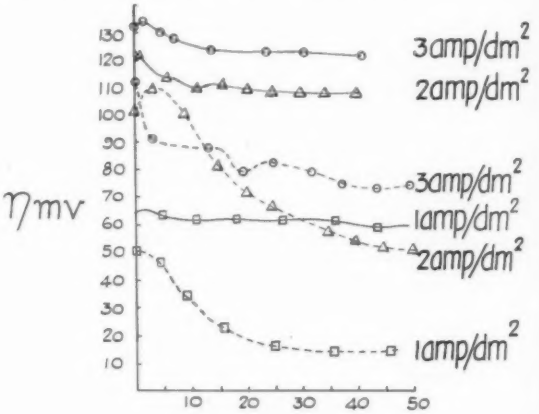


FIG. 5. S_{Low} and S_{High} at various current densities.—— S_{High}, - - - - S_{Low}.

with areas of coarse structure in the upper region, and the C.S.P. value fell below 100 mv. Daily checks revealed a gradual increase in the proportion of coarse deposit, the fine deposit becoming restricted to the lower edge of the cathode, until after 10 days the deposits were coarse throughout, the solution then appearing to be quite stable with a C.S.P. value of 55 mv at 2.0 amp/dm². Tests performed at 1.0, 2.0, and 3.0 amp/dm² showed that the difference between the C.S.P. values of fresh and old solutions was about 50 mv at each current density (Fig. 5). Similar differences were obtained with solutions 125 g/l $CuSO_4 \cdot 5H_2O$ and 100 or 150 g/l H_2SO_4.

These results suggested that the electrolyte was unstable, and that the C.S.P. value depended on the previous history of the solution. There seemed to be two extremes, the initial state yielding at 2.0 amp/dm² a C.S.P. value of 110 mv and a fine deposit,

and the final state with C.S.P. value 55 mv and giving a coarse deposit. Solutions which approximate to the former will be denoted "S_{High}" and those with the latter characteristics "S_{Low}". Intermediate conditions give a mixture of coarse and fine deposits of relative areas corresponding with the C.S.P. values. After suitable etching, sections were examined microscopically and it was confirmed that the crystal grains themselves were coarse and fine in accord with the gross surface appearance. This instability of the solution is probably the main factor in explaining the lack of accord between the results of various workers in this field.

Effect of Repeated Use of the Solution

Gauvin and Winkler used their solutions once only, but the reason was not made clear. In a $CuSO_4$-H_2SO_4 solution containing no addition agents the effect of dissolved oxygen is such that the copper concentration will be increased and the sulfuric acid concentration decreased on repeated electrolysis (11), but owing to the high concentrations of the reagents present it seemed improbable that these slight concentration changes would affect appreciably the polarization values.

Electrolysis of a batch of S_{Low} was, therefore, allowed to proceed until the C.S.P. value was attained. The electrolyte was then removed from the cell and reused with a fresh cathode base, when the C.S.P. value had increased to 74 mv and the deposit was heterogeneous, an area of fine structure appearing low on the cathode. A third usage of the solution led to a C.S.P. value and deposit identical with those obtained with S_{High}. These results (Fig. 6) are typical, although frequently one run of 50–60 minutes was adequate to convert S_{Low} to S_{High} whereas in some cases as many as four usages were needed. The dotted curve in Fig. 6, showing the result of a fourth usage of S_{Low}, indicates a result often observed when the persistence of the coarse deposit was pronounced; such rise and fall in the curve was sometimes observed with S_{Low} which had stood for some months. A second usage of S_{High}, on the other hand, produced only an increase of 5–7 mv in the C.S.P. value, and further usage produced no further effect.

The stability of S_{High} produced by the electrolysis of S_{Low} was surprisingly high, samples showing no sign of reversion after keeping in sealed bottles at 25°C for a year.

The fact that S_{Low}, produced by keeping S_{High} at 30° C, was converted back to S_{High} by repeated electrolysis suggested that its properties were abnormal owing to the presence of an impurity which was removed by electrolysis. The effect of addition agents in raising the cathode polarization potential and in producing finer deposits is well known, but little reference to any compounds with the reverse effect is to be found. Marble (12) observed that a few addition agents increased the grain size of copper and Lloyd, Lauver, and Hovorka (13) observed both maxima and minima of polarization potential when varying concentrations of some addition agents were used in copper nitrate baths. That the S_{High} is not formed from S_{Low} by the production or entry into the solution from the anode of an impurity possessing the normal "addition agent" action was proved by the fact that results identical with those described were obtained when spectroscopically pure copper was used as anode.

Effect of Atmospheric Gases

The important effect of dissolved oxygen upon the Cu^{++}–Cu^{+} system in the discharge process is well recognized, as is the fact that the reduced cathode efficiency in copper electrorefining cells is due largely to the chemical oxidation of cuprous to cupric ion, and the electrolytic reduction of cupric ion to cuprous to maintain the equilibrium. However, this equilibrium and the effect of oxygen upon the cuprous ion have been largely disregarded in investigations of the polarization of copper in acid copper sulfate solutions, although Erdey-Gruz and Volmer (14) worked under inert atmospheres in studying the polarization in copper sulfate solutions without added acid.

As the concentration of oxygen in the water would vary with the storage temperature, this appeared to be a possible factor in determining the nature of the deposit, and hence the effect of working with oxygen-free solutions under inert atmospheres was studied. S_{High} was boiled and allowed to cool under oxygen-free nitrogen before being transferred to the Haring cell in an atmosphere of the same gas, but the results were identical with those obtained with S_{High} treated in the usual way. However when nitrogen had been passed through S_{Low} for 1½ hours before electrolysis under the same gas, the initial polarization values were similar to those associated with S_{Low}, but after about 5 minutes the polarization potential increased and the final C.S.P. value was equal to that obtained with S_{High}; the deposit was heterogeneous (Fig. 7, curve *A*). After treatment with nitrogen for 12 hours the whole curve resembled that obtained with S_{High} (curve *B*), whether the electrolysis was conducted in air or in a nitrogen atmosphere. Subsequent passage of oxygen through the solution did not affect the C.S.P. values or the crystalline character of the deposit, showing the change to be due to the passage of nitrogen, although the time of such treatment necessary to cause the conversion was somewhat variable; with some solutions treatment for 12 hours caused an increase in

the C.S.P. value of only 10–15 mv. These results suggest that in certain cases, at least, the properties of S_{Low} are due to a volatile impurity removed by nitrogen treatment. This view is supported by the fact that in some cases boiling the solution for about 30 minutes converted S_{Low} into S_{High}, whereas, with other samples, refluxing for several hours produced little effect.

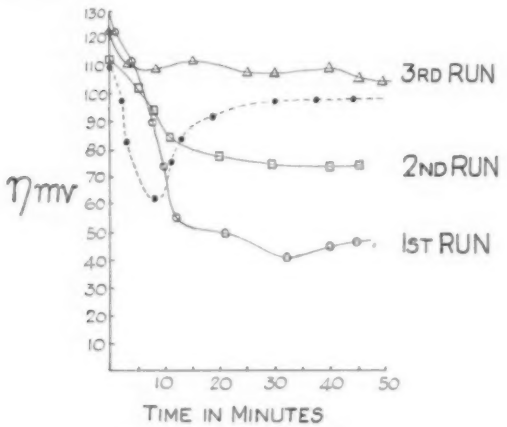


FIG. 6. Repeated runs of S_{Low}

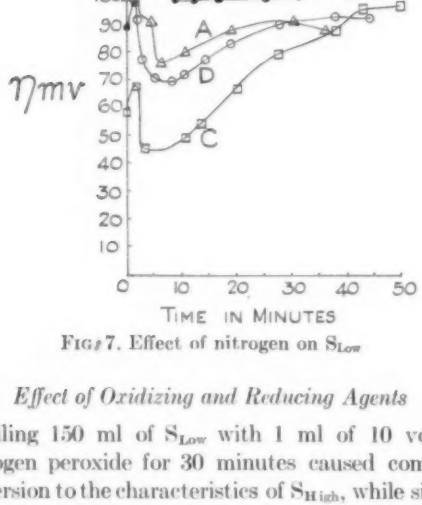


FIG. 7. Effect of nitrogen on S_{Low}

Effect of Oxidizing and Reducing Agents

Boiling 150 ml of S_{Low} with 1 ml of 10 volume hydrogen peroxide for 30 minutes caused complete conversion to the characteristics of S_{High}, while similar treatment had no effect on S_{High} itself. Nitric acid had a similar effect. This treatment with oxidizing agents was the only method which gave complete conversion in all cases.

In view of this result it seemed possible that small quantities of reducing agents might produce the reverse change, but the addition of various concentrations of ferrous sulfate, hydrazine sulfate, hydroxylamine, and glucose produced no effect upon either the C.S.P. value or the nature of the deposit obtained with S_{High}. Sulfur dioxide, however, had a pronounced effect, but only when added in appreciable quantities; S_{High} saturated with sulfur dioxide had the properties of S_{Low}, but addition of 1 ml of saturated sulfur dioxide solution to 150 ml of S_{High} produced no effect.

These results appeared to negate the view that the interchange was based upon oxidation-reduction reactions, and to indicate that the C.S.P. and crystal nature of the deposit are not affected by disturbing the Cu^{++}–Cu^{+} ionic equilibrium. That the change in the nature of the deposit and in the C.S.P. value on repeated electrolysis of the solution was not due to the gradual attainment of an equilibrium concentration of cuprous ion in the solution was confirmed by shaking S_{Low} with spongy copper, produced by electrolysis at high current density. After this treatment the solution yielded almost exactly the same C.S.P. value as an untreated sample.

TABLE II. *Effect of the purity of the water upon the variation of the constant state polarization potential with time*

Nature of water	η at 2 amp/dm² (mv)						
	Time in days						
	0	2	8	14	16	20	30
Laboratory distilled water	100	48	48				
Distilled water as used for the manufacture of electrolytic condensers	105			79		55	
Conductivity water	98	98	92	81		53	
Freshly redistilled water	105	100	97		97		66
Water distilled from potassium permanganate and sodium hydroxide	105	100	97			97	66

Effect of Purity of the Water

If the effect were due to contaminants the most probable source was the distilled water. Therefore solutions were prepared using water from various sources and kept at 25.0°C, in glass bottles, their C.S.P. values being checked periodically. The results (Table II) show that the stability depended upon the purity of the water, thereby explaining the variable behavior observed initially when solutions were kept. However, in no case was the purification of the water, without attention to other factors, sufficient to prevent a slow change in the result given by the solution.

Preparation of a Stable Solution

As a result of the information obtained in this investigation the procedure adopted to make a stable solution was to use "AnalaR" sulfuric acid, copper

sulfate twice recrystallized from freshly distilled water containing a little sulfuric acid, and water freshly distilled from potassium permanganate and sodium hydroxide. After preparation the solution was boiled, cooled in a stream of nitrogen, and then stored in a glass-stoppered flask in a nitrogen atmosphere. Solutions prepared in this way gave high polarization values and fine crystal structure. They were quite stable and could be retained for months without showing any tendency for coarse structure areas to develop in the cathode deposits.

Discussion

After this work was completed it was noted that a similar instability of the solution had been observed by some other investigators. Thus Foerster (15) showed that more accurate results were obtained with a copper coulometer after the solution had been submitted to several hours' electrolysis at 100°C. This was attributed to the formation of cuprous ion through the partial discharge of cupric ions. Also Marie and Thon (16), while studying the stress in copper deposits, found that they did not get reproducible results unless freshly prepared solutions were used.

Again, Jacquet (17) found that the adhesion values of electrodeposits obtained from an acid copper sulfate solution changed during the operation of the bath. This aging effect was attributed to the progressive enrichment of the electrolyte in cuprous ions. Hothersall (18) queried Jacquet's conclusions, pointing out that the theory could be tested by studying the effect of oxidizing agents on the aged solutions or of copper powder on the fresh solution.

In a later publication (19) Jacquet reported that this aging also affected the crystal structure of the deposit. Using a fresh solution he obtained striated deposits and these became uniform on repeated electrolysis. In discussing this paper, Hothersall (20) mentioned that he had found a variation in the hardness values which were unaffected by equilibrating with copper powder. He pointed out that copper sulfate solutions are very sensitive to minute traces of impurity, and that the characteristics of the deposit can be changed by contact of the solution with filter paper or rubber tubing. This effect could generally be remedied by boiling with a small quantity of permanganate and, after filtering through sintered glass, discharging the pink color with hydrogen peroxide, although the method was not always successful, as certain organic materials are not destroyed by this process.

Ollard (21) pointed out that a freshly made solution gives a sandy deposit of copper, having much larger crystals than are deposited from one which has been working for some time, although the chemical compositions appear to be identical.

These observations are all in accord with those obtained in the present investigation, the solutions used by Gauvin and Winkler and the fresh solutions of Jacquet being similar in character to those which have been denoted S_{Low}. The present work has shown, however, that Jacquet's explanation is untenable.

The fact that baths have to be "run in" is a well-known empirical fact in electroplating, and, consequently, some observations made regarding the electrodeposition of other metals may be relevant to the present issue. For instance, Clark (22) found that the deposits obtained from fresh cadmium cyanide solutions were very porous, and their porosity disappeared only with the aging of the solution. Again, while studying the silver coulometer, Rosa, Vinal, and McDaniell (23) found that the deposits obtained were frequently imperfectly crystalline and distinctly striated. These deposits were heavier than those obtained when the deposit was normally crystalline, and it was found that the filter paper used for enclosing the anode was responsible for the effect. Repeated electrolysis of the contaminated solution caused the deposit to become less striated and finally free from striations. The filter paper and extracts from it were found to have a reducing effect on the solution, so the production of the striations was considered to be associated with the presence of a reducing impurity and simultaneous motion of the electrolyte over the cathode.

The results which have been obtained in the present investigation are all compatible with the supposition that the properties of S_{Low} are due to the presence of a very slight trace of impurity, formed during the storage of the solution, which has the unusual property of reducing the C.S.P. value and increasing the crystal size of the deposit. The formation of this impurity appears to be dependent upon the presence of some foreign matter in the materials used, and occurs the more rapidly the higher the temperature at which the solution is stored. The impurity is removed by repeated electrolysis of the solution, by oxidizing agents, and sometimes by boiling or passing nitrogen gas through the solution. It seems, therefore, to be destroyed by oxidation and, in some cases, to be of a volatile nature.

This evidence suggests that the active impurity is a very small trace of some oxidizable material. In a future communication details will be given of the effects of compounds which simulate this phenomenon, concentrations of the order of $0.0001M$ being adequate in most cases to transform completely S_{High} to S_{Low}. Such compounds include hydrogen sulfide, carbon disulfide, thiourea, and sodium thiosulfate. It is of interest to note that these are all

sulfur compounds, and it is conceivable that the degradation of S_{High} to S_{Low}, with the accompanying change in the character of the deposit, may be due to the formation of traces of compounds of this type by bacteriological or ordinary chemical reactions favored by high storage temperatures. Porges (24) found that jelly-like molds can form in acid copper sulfate solutions and have a deleterious effect upon the deposits and it does not seem to be impossible for such molds to develop in traces without being obviously visible. Oxidation of the solution presumably converts these compounds into products which do not affect the polarization characteristics.

More than one such reduction product seems to be formed, as in some cases boiling the solution for a short time, or passage of nitrogen, removed the effect completely, indicating a volatile impurity of the type of hydrogen sulfide or carbon disulfide, whereas in other cases little effect was produced by this treatment, as would be expected if the impurity were of the type of thiourea or thiosulfate.

The failure of previous investigators in attempting to obtain reproducible results is attributable to the operation of these factors, in addition to the variation of experimental technique.

Any discussion of this paper will appear in a Discussion Section, to be published in the December 1951 issue of the JOURNAL.

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Electrodeposition of Metals from Fused Quaternary Ammonium Salts[1]

FRANK H. HURLEY[2] AND THOMAS P. WIER, JR.[3]

Department of Chemistry, The Rice Institute, Houston, Texas

ABSTRACT

Electrolytic studies on fused mixtures of ethyl pyridinium bromide and metallic chlorides have shown that the following metals can be deposited on the cathode: Ag, Cu, Bi, Pb, Sn, Ni, Co, Cd, Fe, Zn, and Al. Tests involving metallic sulfates and nitrates, as well as mixtures employing fused benzyl pyridinium bromide, showed that these metals can be deposited except in cases where nonionic complex compounds are formed.

In more extensive studies of the properties of aluminum chloride dissolved in fused ethyl pyridinium bromide it was found from melting-point data that a compound having the composition $EtPyBr \cdot AlCl_3$ is formed, and that a very low-melting eutectic (−40°C) occurs at 67 mole per cent $AlCl_3$. Aluminum could be deposited from mixtures in the composition range 54–70 mole per cent $AlCl_3$. Smooth plating of aluminum on iron, steel, copper, bronze, brass, platinum, lead, and tin could be accomplished by using an aluminum anode. The best plates were obtained when the composition of the bath was in the immediate neighborhood of the eutectic composition and at a temperature of 125°C, using a current density of 0.5 amp/dm². Similar results were obtained using $AlCl_3$ and ethylene dipyridinium dibromide mixtures.

The state of ionization of the compound $EtPyBr \cdot AlCl_3$ in benzene solution was investigated by means of migration and conductivity experiments.

I. Behavior of Pyridinium Halides and Metallic Salts

Electrolytic studies of quaternary ammonium salts have shown these salts to be good conductors and to behave in general like inorganic salts. Studies of mixtures of these salts with true inorganic salts are not, however, very numerous. Audrieth, Long, and Edwards (1, 2) examined qualitatively the solubility of various metals, oxides, and salts in fused pyridinium chloride (pyridine hydrochloride). Many of the resulting melts conducted the electric current readily and the less active metals could be readily deposited on the cathode by electrolysis. They were unable to obtain deposition of the more active metals. The acidic nature of the pyridinium ion imposes a serious limitation on such electrodeposition, a limitation which would not be present in pyridinium salts in which the hydrogen atom causing the acidity is replaced by an alkyl or aryl group.

Several *N*-substituted pyridinium halides were prepared by the reaction of pyridine and an alkyl or aryl halide and their suitability for use as fused electrolytes studied. The compounds examined were ethyl pyridinium bromide and chloride, butyl pyridinium chloride, benzyl pyridinium bromide and chloride, and ethylene dipyridinium dibromide and dichloride.

Mixtures of various anhydrous metallic chlorides with fused ethyl pyridinium bromide were electrolyzed using a platinum cathode and a carbon rod anode. The temperature of the molten mixtures was held at 135° ± 5°C. Voltages between 6 and 12 volts were employed. Metallic deposits were obtained at the cathode with mixtures containing the following metallic ions: silver, cupric, bismuth, lead, stannous, nickel, cobalt, cadmium, ferric, zinc, and aluminum. No deposit could be obtained from mixtures containing manganous chloride, although this salt was found to be quite soluble in fused ethyl pyridinium bromide. The chlorides of sodium, lithium, barium, and cerium were practically insoluble in the melt. An electrolysis of a mixture containing beryllium chloride produced a thin brownish coating on the cathode.

A similar but less comprehensive series of experiments was performed using metallic sulfates and nitrates in fused ethyl pyridinium bromide. The results of these tests are in general agreement with the chloride series, but it should be noted that the sulfates of the metals were in most instances much less soluble than either the chlorides or nitrates.

The behavior of the ethyl pyridinium ion in these electrolysis experiments is of considerable significance. In the absence of added salts, fused ethyl pyridinium bromide conducts very well, producing

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[2] Present address: Reed College, Portland, Oregon.

[3] Present address: Shell Oil Company, Houston, Texas.

bromine at the anode and a characteristic dark blue reduction product at the cathode. Although this material was not positively identified, it is probably diethyldihydro-dipyridyl (3). In the electrolysis of the salt mixtures this same material appeared along with the metallic deposit in most of the experiments but was strikingly absent when relatively high concentrations of the following chlorides were used: stannous, cobalt, ferric, zinc, and aluminum. This fact, accompanied by the observation that a number of the colorless inorganic chlorides formed deeply colored solutions when dissolved in the fused pyridinium salt, suggests that metallic ions probably form coordination complexes with ethyl pyridinium bromide.

A short series of electrolytic experiments was performed using fused benzyl pyridinium bromide as the solvent. These tests gave quite different results. Mixtures with nickel chloride hardly conducted the current at all. Cupric chloride in low concentration gave a clean deposit of metallic copper, but in high concentration showed a very low conductivity and produced no deposit. Cadmium chloride behaved similarly but gave no metallic deposit at all. Lead and zinc could be deposited, but their solutions were of much lower conductivity than in previous experiments. These results make it appear that nonionic complex compounds may be formed by reaction between some of the metallic chlorides and *N*-substituted pyridinium halides.

II. Electrodeposition of Aluminum

The special interest which attaches to the problem of the electrodeposition of the light metals suggested the desirability of making a more careful study of the deposition of aluminum from *N*-substituted pyridinium salts. A number of studies on the electrodeposition of aluminum from organic mixtures have been reported (4), but the only process which is similar to the fused pyridinium salt mixture is that of Keyes and Swann (5), which employs an electrolyte consisting of aluminum bromide and tetraethyl ammonium bromide. According to these investigators, deposition of aluminum from this mixture can be best accomplished at a temperature of 100°C and a current density of 0.068 amp/cm². Under these conditions a potential of 22.6 volts must be applied.

Composition of electrolyte.—The first step in the study of the aluminum deposition consisted of an examination of the composition of the electrolyte mixture as it related to physical properties. It was found (6) that the aluminum chloride-ethyl pyridinium bromide system gives a simple melting-point diagram showing two eutectic mixtures and a compound corresponding to a 1:1 mole ratio of $AlCl_3$ to EtPyBr. The diagram is shown in Fig. 1. The two eutectics appear at almost exactly 1:2 and 2:1 mole ratios of $AlCl_3$ to EtPyBr. These eutectics have melting points of 45° and −40°C respectively. The melting point of the 1:1 compound is approximately 88°C. All mixtures containing less than 50 mole per cent of $AlCl_3$ were orange-colored. The color of the mixtures changed from bright orange to deep red very sharply between 50 and 55 mole per cent $AlCl_3$ and then darkened to gray-brown as the 2:1 eutectic composition was approached. The colors of these solutions coupled with the behavior of the mixtures on electrolysis suggest that complex compounds are involved.

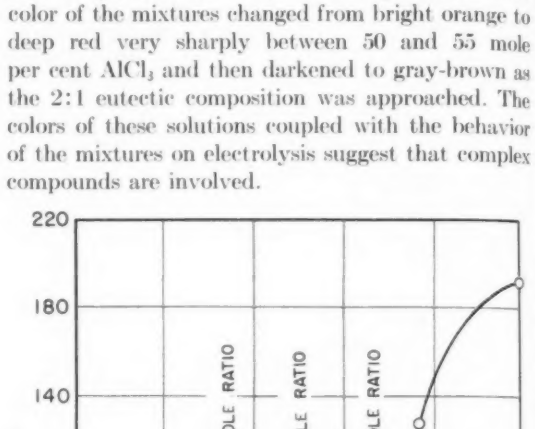

Fig. 1. Phase diagram of the system aluminum chloride-ethyl pyridinium bromide.

Electrolytic experiments were performed on mixtures of varying composition using a small (1 in. diameter) glass cell with a cylindrical aluminum anode which surrounded a small flat cathode made of iron, steel, or copper. The cell was immersed in an oil bath and kept at 120°–130°C during the experiments. In cells of this design, voltages of 2–3 volts (or less) were customary. The principal result of these experiments was to establish the fact that the optimum composition for electrodeposition of aluminum is that of the low-melting eutectic mixture, which contains two moles of $AlCl_3$ per mole of EtPyBr. Smooth, shiny, adherent plates of aluminum were obtained with this composition, whereas electrolytes containing either more or less aluminum

chloride produced less satisfactory plates. The composition range for satisfactory plates is approximately 54–70 mole per cent $AlCl_3$. At 77 mole per cent $AlCl_3$ a dark gray, nonadherent deposit was obtained. At 50 mole per cent (corresponding to the compound), electrolysis yielded no deposit on the cathode, and with less aluminum chloride, only the characteristic blue reduction product was formed.

Less comprehensive studies were made on electrolytes consisting of aluminum chloride mixed with either ethylene dipyridinium dibromide or ethylene dipyridinium dichloride. Both types of mixtures showed characteristic low-melting eutectics at compositions corresponding to four moles of $AlCl_3$ per mole of pyridinium salt, and these eutectics proved to give the most adherent and satisfactory deposits of aluminum on electrolysis. It thus appears that these systems resemble closely the $AlCl_3$-EtPyBr system and that the 2:1 mole ratio of $AlCl_3$ to substituted pyridinium nucleus is characteristic for satisfactory electroplating of aluminum.

Effect of temperature.—Experiments with fused mixtures of aluminum chloride with each type of alkyl pyridinium halide showed the expected behavior: the conductivity increased linearly with increasing temperature.

Since pyrolytic decomposition of the pyridinium salts occurs at high temperatures, it was of interest to find the lowest temperature at which satisfactory aluminum deposits could be obtained. For the ethyl pyridinium bromide mixture the 2:1 eutectic proved to be the best. About 125°C was optimum, but smooth, adherent plates could be obtained at as low as 40°C, although at this temperature the usable current density was quite low, and the deposits were almost white.

Current density.—Results of a study of the effect of the current density on the character of the aluminum deposit may be summarized as follows. At a current density of 0.5 amp/dm², the aluminum plate on a steel cathode was uniform and shiny and, therefore, this is taken to be the optimum plating condition. Above this current density the deposits began to lose their shiny character and when the current density reached 1.0 amp/dm² they were gray and somewhat coarse. The maximum length of the electrolysis was found to be approximately 0.5 amp-hr /dm². When the electrolysis was continued for a longer period the edges of the deposit became crystalline.

Contamination and deterioration of the plating bath.—As one would expect, an aluminum chloride-pyridinium salt bath is hygroscopic and, therefore, must be afforded some protection from moisture. This can be provided by the passage of a slow stream of dry gas through the cell. If the bath does absorb moisture, as may be the case during its preparation, electrodeposition of aluminum is impossible until the acid liberated by the hydrolysis of the water has been removed. A simple way to accomplish this is to allow the electrolyte to react with a piece of metallic aluminum before beginning the use of the bath.

A related problem arises from the absorption of moisture by the electrolyte which clings to the surface of the cathode when it is removed on completion of the electrolysis. Again, acid is produced by hydrolysis and the aluminum plate is attacked by the acid. This difficulty can be overcome by rinsing the cathode immediately in benzene or toluene, followed by rinsing with water.

The bath is somewhat sensitive to metallic impurities. Small amounts of metallic ions such as iron and copper, when added to the electrolyte, caused the deposits to become black and nonadherent.

It was also found that the plating properties of the bath deteriorated with time and eventually satisfactory plates of aluminum were impossible to obtain. Numerous experiments led to the conclusion that this is brought about almost entirely by oxidation in air. Therefore, the bath had to be operated in an atmosphere of a dry, nonoxidizing gas to avoid this deterioration.

State of ionization of electrolyte mixture.—The phase study of the two-component system $AlCl_3$-EtPyBr showed the existence of a compound having the empirical formula $AlCl_3 \cdot EtPyBr$. The low-melting eutectic most often employed in these experiments has a composition corresponding to equimolar amounts of this compound and $AlCl_3$. It is of interest to inquire into the state of ionization of the components of this mixture.

The ionization of the aluminum chloride presumably follows a step-wise pattern according to the following scheme:

$$AlCl_3 \rightleftarrows AlCl_2^+ + Cl^- \rightleftarrows AlCl^{++} + 2Cl^- \rightleftarrows Al^{+++} + 3Cl^-.$$

For the compound $AlCl_3 \cdot EtPyBr$, two possibilities for dissociation present themselves as likely:

$$AlCl_3 \cdot EtPyBr \rightleftarrows \underset{\text{(as indicated above)}}{AlCl_3} + \underset{[EtPy]^+ + Br^-}{EtPyBr} \qquad (I)$$

and

$$AlCl_3 \cdot EtPyBr \rightleftarrows [AlCl_3 \cdot Br]^- + [EtPy]^+. \qquad (II)$$

If the compound ionizes according to (I) above, all the ionized aluminum in the eutectic mixture will be in the cations. However, if the ionization follows pattern (II), some of the aluminum in the mixture will be present in a complex anion. In this case it would be possible for aluminum to move toward

both the anode and cathode during electrolysis. It will be noted that, in either case, the ethyl pyridinium ion can exist in the solution.

If the addition of a solvent does not introduce molecular reactions, it would be possible to gain the desired information by means of migration experiments. Benzene appeared to be a suitable solvent.

TABLE I. *Migration analysis results (anode compartment)*

	Before electrolysis moles/g electrolyte	After electrolysis moles/g electrolyte	Total change moles
Al	1.645×10^{-3}	1.681×10^{-3}	$+0.71 \times 10^{-3}$
Cl	4.761×10^{-3}	4.863×10^{-3}	$+2.02 \times 10^{-3}$
Br	1.563×10^{-3}	1.596×10^{-3}	$+0.65 \times 10^{-3}$

TABLE II. *Comparison of observed and theoretical changes*

	Experimental	Theoretical
$\frac{\text{Change in Cl}}{\text{Change in Al}}$	2.85	3
$\frac{\text{Change in Br}}{\text{Change in Al}}$	0.92	1
$\frac{\text{Change in Cl}}{\text{Change in Br}}$	3.10	3

To this end a solution of the following composition was prepared in an atmosphere of dry nitrogen:

$AlCl_3$ = 21.92 wt % (based on Al analysis)
EtPyBr = 29.60 wt % (based on Br analysis)
Benzene = 48.48 wt % (by difference)

This solution (corresponding to $AlCl_3 \cdot EtPyBr$ with a 1 per cent excess of $AlCl_3$, saturated with benzene) was placed in an electrolysis apparatus of the Hittorf type used for the determination of transference numbers. The anode was copper and the cathode iron. A current of 0.04–0.05 amp was passed for 35 minutes. During this time the blue organic reduction material was produced in the cathode compartment and a white solid (probably a copper salt) in the anode compartment. At the end of the electrolysis the contents of the anode compartment (including the salt formed) were withdrawn into a weighed bottle for analysis.

Analyses[4] were made for changes in the concentration of aluminum, bromide, and chloride in the anode compartment. Aluminum was determined by the 8-hydroxy quinoline method of Berg, total halide by the Volhard method, and bromide in the presence of chloride by the differential oxidation method of Kolthoff and Yutzy (7).

The analytical results and the corresponding total change in the amounts of aluminum, bromide, and chloride in the anode compartment are shown in Table I.

The ratios of the observed changes are compared with the stoichiometrical ratios to be expected according to pattern (II) in Table II.

These results indicate very strongly the prevalence of pattern (II) for the ionization of the molecular compound $AlCl_3 \cdot EtPyBr$ in benzene solution.

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The Electrodeposition of Aluminum from Nonaqueous Solutions at Room Temperature[1]

FRANK H. HURLEY[2] AND THOMAS P. WIER, JR.[3]

Department of Chemistry, The Rice Institute, Houston, Texas

ABSTRACT

The electrodeposition of aluminum in the form of white or shiny adherent plates on various metals has been accomplished at room temperature. A satisfactory plating solution is prepared by mixing two moles of anhydrous aluminum chloride with 1 mole of ethyl pyridinium bromide, preferably in a dry, oxygen-free atmosphere, to produce a liquid to which benzene (or toluene) is added until a second layer, principally excess benzene, forms on the top of the plating solution. Using an aluminum anode, plating may be carried out in a protected atmosphere at cathode current densities of approximately 1 amp/dm^2 (about 9 amp/ft^2) using voltages of the order of one volt.

The use of an alternating current superimposed on the direct plating current (*a*) greatly improved adherence, e.g., a copper wire plated by this procedure can be repeatedly flexed without breaking the coating; (*b*) increased thickness without brittleness; (*c*) increased maximum current density; (*d*) somewhat lowered the voltage requirement; (*e*) gave the same efficiency based on the direct current; and (*f*) changed the appearance from shiny to satiny.

INTRODUCTION

Methods for the electrodeposition of aluminum on other metals were developed by various investigators some years ago (1, 4, 5, 6). The authors have shown that aluminum can be deposited electrolytically on other metals from solutions of anhydrous aluminum chloride in any one of several fused pyridinium compounds. Operation at room temperature was found possible by the addition of any one of several organic solvent reagents to the mixture of aluminum chloride and one of the pyridinium compounds (7).

EXPERIMENTAL

The most important and useful system was the 66.7 mole per cent aluminum chloride (as $AlCl_3$)-ethyl pyridinium bromide eutectic mixture. Such materials as pyridine, benzene, toluene, xylene, petroleum ether, kerosene, gasoline, ethyl ether, carbon disulfide, chloroform, alkyl halides, and chlorobenzene were examined with respect to their ability to form a suitable solution with the eutectic mixture. Of these, the aromatic hydrocarbons proved to be the most satisfactory. The addition of dry benzene to the aluminum chloride-ethyl pyridinium bromide eutectic in amounts from 20 to 50 per cent by volume produced clear, light brown solutions with no evolution of heat. When an amount of benzene approximately equal to the amount of eutectic had been added a clear, less dense layer formed. The second layer consisted almost entirely of benzene.

Electrolysis of benzene solutions showed that aluminum could be deposited from these at room temperature. Furthermore, the plates were smoother and shinier than those obtained from a fused bath containing no benzene. Toluene and xylene showed similar results.

Effect of Aluminum Chloride Concentration

Several solutions of aluminum chloride in ethyl pyridinium bromide were saturated with toluene and the electrolyte layer of the resulting solutions electrolyzed to determine the range of concentrations suitable for the electrodeposition of aluminum. It was observed that the range of aluminum chloride concentrations from which aluminum can be deposited is limited. The actual value for the minimum lies between 50.0 and 58.6 weight per cent aluminum chloride in the starting mixture. At concentrations much below 50.0 weight per cent of aluminum chloride, a blue organic water soluble deposit is obtained which is believed to be diethyldihydrodipyridyl produced by the reduction of the ethyl pyridinium ion. An upper limit also exists in the region of 60 to 63 per cent by weight aluminum chloride (on the basis of the two-component mixture before the addition of toluene), due principally to the occlusion of aluminum chloride in the deposit.

Thus, the range of concentrations with which plating can be carried out is narrower than was observed for the fused mixtures. An understanding of the narrow limits of concentration with which plat-

[1] Manuscript received December 4, 1950.

[2] Present address: Reed College, Portland, Oregon.

[3] Present address: Shell Oil Company, Houston, Texas.

ing can be carried out is facilitated by a discussion of the phase relationships of this system.

Phase Relationships of the System Aluminum Chloride-Ethyl Pyridinium Bromide-Toluene

An approximate phase diagram of the system ethyl pyridinium bromide-aluminum chloride-toluene at a temperature of 30°C is presented in Fig. 1. The system is rather complicated and has not been thoroughly investigated.

In area A, the three components exist as a single liquid phase which varies from light yellow-brown to deep red in color depending upon the composition.

In area B, two liquid phases are in equilibrium. The composition of the colored, more dense phase is given by the line separating areas A and B. The composition of the clear, colorless, less dense phase was

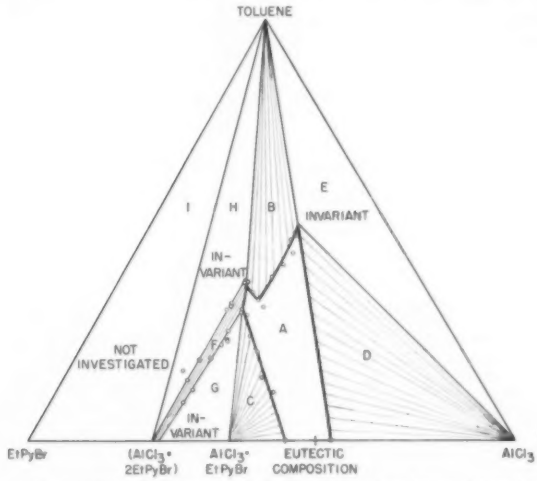

FIG. 1. Phase diagram of the system: aluminum chloride-ethyl pyridinium bromide-toluene at 30°C. Compositions expressed as weight per cent.

found to be greater than 99 per cent by weight toluene, which allows it to serve as a protecting layer above the electrolyte. The line between areas A and B is the most important line on the diagram from a practical standpoint as it determines the composition of the electrolyte layer of the solutions which can be used for plating. Practical plating is restricted to a narrow portion of this curve on either side of its intersection with an imaginary line connecting the toluene apex with the point marked "eutectic composition" on the lower side of the triangle.

The other areas of the diagram are not of value for plating purposes but serve to illustrate the nature of the system.

Types of Aluminum Plates

In studying the types of plates obtainable on iron or brass at various current densities, thin strips of these metals 2.5–3.8 cm wide were used. These were inserted in the electrolyte layer to a depth of 3–5 cm. The electrolytic cell consisted of a wide-mouth, cylindrical jar 5.2 cm in diameter and 12.5 cm deep. The cell was closed with a tight fitting, coated wood top slotted to allow insertion of the cathodes. The slot was covered by a spring-activated, sliding plate which also served to hold the cathode strip in place during a plating operation. The top was also fitted with inlet and outlet tubes so that dry air (later dry nitrogen) saturated with toluene or benzene could be passed slowly through the cell to provide positive outward displacement when the slot was open. A single aluminum anode was used in the form of a cylindrical sheet 0.025 cm thick, 5 cm high, and 15 cm in circumference. The electrolyte was a 58.6 per cent by weight $AlCl_3$-ethyl pyridinium bromide eutectic mixture saturated with benzene or toluene. Using 100–125 cm^3 of this solution, the cell was filled to approximately 5 cm. An additional 1 cm layer of benzene or toluene served as a protective cover.

Prior to use, the cathodes were merely sanded with emery paper, etched with 6*N* hydrochloric acid, and dried.

The voltage during plating was usually quite low, of the order of one volt.

A survey of plates made at different current densities and with different individual bath preparations revealed that the best current density for plating varied between 0.5 and 2.0 amp/dm^2 depending on observance of certain precautions during use and preparation of the baths. These precautions will be discussed in a later section. As a result, in the following discussion current densities are referred to as being high or low compared to the then existing value for shiny plates.

The maximum current density found suitable for these baths is considerably higher than that found to be the maximum for the electrodeposition of aluminum from the fused bath of aluminum chloride and ethyl pyridinium bromide at temperatures of around 125°C. The plates from the bath saturated with toluene or benzene at these current densities were remarkably shiny and very uniform (see Fig. 2*a* and 2*b*). In general, they were much smoother, more uniform, and shinier than the plates from the fused bath.

At current densities somewhat lower than those for shiny plates, the plates were white and showed more diffuse reflection (see Fig. 3*a* and 3*b*). Very low current densities produced plates which were gray, very coarse, and not very coherent or adherent.

As the current density was raised above the value at which shiny plates were obtained, brown striations of an unknown (apparently organic) nature began to appear on the shiny deposit. At slightly

higher current densities, "burned" areas (bare areas bordered in black) appeared on the edges of the plate. At very high current densities the deposits were heavy, black, and nonadherent, and seemed to contain occluded aluminum chloride or electrolyte. They reacted vigorously with water.

The plates adhered well under rubbing or polishing if the sheet was not bent. When the shiny aluminum plates on sheets of iron, steel, brass, or copper were

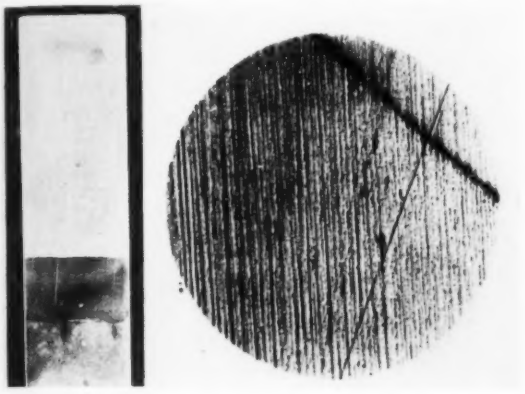

FIG. 2. Normal photograph (*a*) and 100× photomicrograph (*b*) of a shiny aluminum plate on brass.

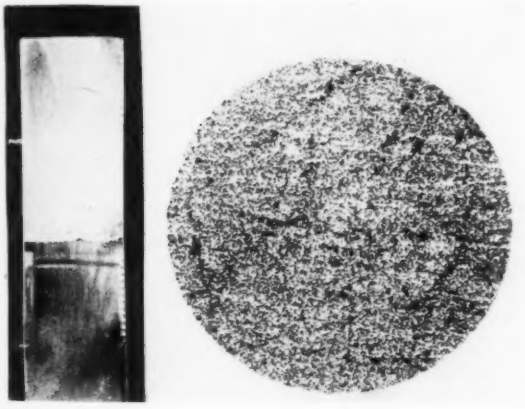

FIG. 3. Normal photograph (*a*) and 100× photomicrograph (*b*) of a white aluminum plate on brass.

bent they were found to be brittle and to buckle on the compression side with resultant flaking off. Since it was also found that the shiny, uniform deposits could be made on cathodes formed in circular and zig-zag shapes, plates would then be satisfactory on objects of odd or irregular shape as long as the object was too stiff to be bent. This brittleness was considered a disadvantage. A method by which this may be overcome will be described in a subsequent section.

The thicker the plate the more brittle it was found to be. The usual thickness of the plates was 0.006 mm. Thicker deposits could be obtained readily but this was more than sufficient to give complete coverage. Plates were made as much as 0.025 mm thick but they were somewhat coarser and less uniform. In a subsequent section a method of obtaining better thick plates will be described.

The adherence was somewhat dependent on the preliminary treatment, as would be expected. Plates made on steel without an acid etch were about the same at first as those plates made with an acid etch. However, those which were not acid-etched frequently tended to peel off in a day or so.

Aluminum was plated from this electrolyte on copper, brass, bronze, lead, zinc, nickel, and tin as well as iron. In general, the plates were the same as those on iron. The shiny plates on these metals were also brittle and did not adhere on bending. Zinc, however, was found to be an unsatisfactory base on which to plate because the zinc contaminated the electrolyte easily when in contact with it.

TABLE I. *Cathode current efficiencies with aluminum chloride-ethyl pyridinium bromide-benzene baths*

Current density amp/dm²	Cathode efficiency %
0.21	81.0
0.42	87.2
0.81	88.5
1.00	92.0
1.25	91.9
1.50	91.7
1.51	92.6
1.75	92.0
1.75	91.8

Cathode Efficiencies

In Table I are given the data for the cathode current efficiencies when plating with a "benzene" bath. There is a rise in efficiency of about 7–8 per cent during the first few hours of use of such baths, then the values become constant for a given current density. The values given in the table are for equilibrium conditions. It will be seen from the table that the efficiency increased with current density from 81 per cent at 0.21 amp/dm² to 92 per cent at 1.00 amp/dm². The efficiency then became constant at very close to 92 per cent for the higher current density. This is the reverse of the usual variation of the efficiency with current density, although such a trend is found in some other processes.

Corrosion Resistance

A number of the aluminum plates made on iron, steel, and brass were exposed to the atmosphere for a number of weeks during which there were oc-

casional rains. In one case the exposure was 18 months. After atmospheric corrosion tests the plates on iron showed a few pinholes which were not generally shown by plates made on steel or brass. The pinholes were attributed to the method of surface preparation since only cursory smoothing was attempted. There was no powdering of deposits due to prolonged exposure.

The value of the coatings as corrosion protection was demonstrated by inspection of the unplated portion of the cathodes which had been exposed to the same weather conditions. In every case there was a great deal of heavy rust on both iron and steel whereas the aluminum plated portion retained a shiny appearance and showed only occasional pinholes. Furthermore, these pinholes did not spread and rusting under the aluminum did not take place.

Precautions

When using nonaqueous plating baths there are usually certain precautions to be observed in order to prevent decomposition. Exclusion of moisture and oxygen appear to be necessary to the successful operation of the bath if it is to have a long life. The most important change produced by oxidation in the presence of moisture is a decreased optimum current density. This effect is accompanied by a decreased volume of electrolyte (due to the transfer of part of the electrolyte layer to the upper benzene layer), the appearance of a red color in the solution, and usually the occurrence of a sweet smell. The importance of proper protection against oxygen and moisture is emphasized by the fact that in some instances the optimum current density for an unprotected bath has been observed to decrease as much as 50 per cent in a few days.

Plating with Other Pyridinium Compounds

As mentioned above, certain other pyridinium compounds have been shown to yield mixtures with aluminum chloride from which aluminum can be electrolytically deposited when the mixture is fused. Solvents were added to several such two-component systems and the resulting three-component systems examined. Thus, for example, aluminum was plated at room temperature from the systems: aluminum chloride-ethylene dipyridinium dichloride-toluene or benzene; aluminum chloride-ethylene dipyridinium dibromide-toluene or benzene; and aluminum chloride-ethyl pyridinium bromide-chlorobenzene. For various reasons these systems were not as satisfactory as the one given most attention in this paper. Either the optimum current density was lower or there was more difficulty in preparation of the solution or the direct current conductivities were lower.

Plating With Alternating Current Superimposed on Direct Current

In attempting to use the room temperature plating bath at the maximum possible current density a rapid rise in voltage occurred occasionally and a poor plate resulted. Since mechanical stirring procedures produced a turbulence resulting in a pattern on the cathode, the authors decided to use an alternating current superimposed on the direct current.

Cocks (2) has reviewed work on the use of superimposed alternating current in the electrodeposition of metals, notably gold and nickel, from aqueous solutions, where the alternating current served as a depolarizer. Also, Kameyama and co-workers (3) noted an improvement in the appearance of aluminum plates made from fused baths of inorganic salts when alternating current was superimposed on the direct current, an auxiliary anode being used for the alternating current. With this encouragement, experiments were carried out to test the effect of superimposed alternating current on the organic, nonaqueous aluminum plating baths developed for room temperature operation in this research (8).

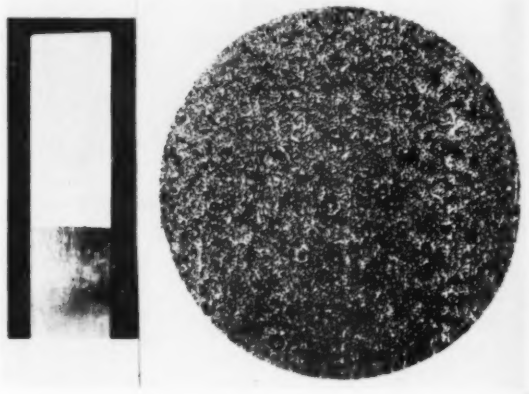

FIG. 4. Normal photograph (*a*) and 100× photomicrograph (*b*) of an aluminum plate made on brass with alternating current superimposed on direct current; a-c(rms)/d-c = 2.

Effect on Appearance of Plates

Plating operations at various ratios of alternating current to direct current showed that the magnitude of the effect increased with increasing a-c/d-c ratio. When plating at near the upper limit of current density, the plates changed in appearance from shiny to satiny and even to white as the ratio was increased. This was more or less typical of many such tests which were made. In all cases, there was no effect on the type of plate unless the maximum value of the alternating current exceeded the value of the di-

rect current. Thus, an actual reversal of the current must occur during a portion of the cycle. A 2:1 to 3:1 a-c (rms)/d-c ratio was optimum.

Photographs and photomicrographs of an a-c/d-c plate at 2:1 a-c (rms)/d-c ratio are presented in Fig. 4*a* and 4*b*. The change in appearance in the plates when alternating current was superimposed may be realized by comparing these pictures with Fig. 2*a* and 2*b* (same d-c current density).

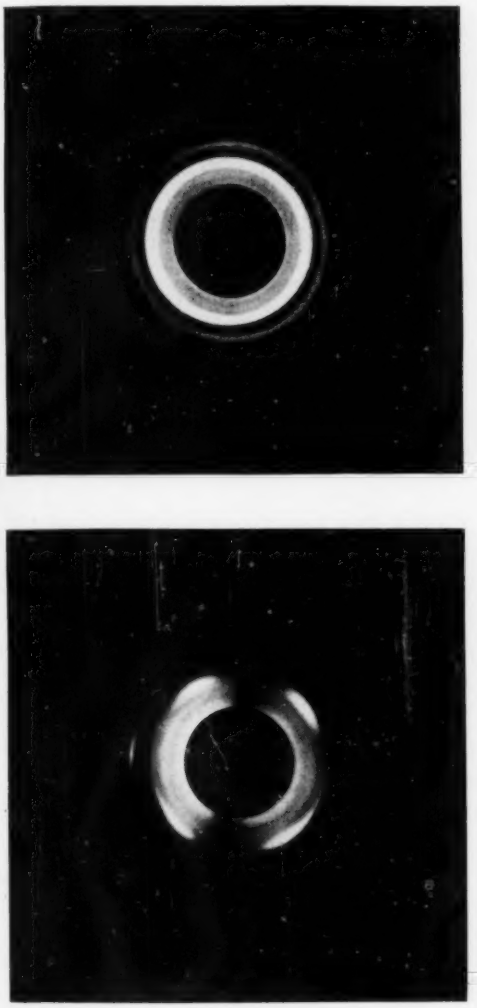

FIG. 5. X-ray diffraction pictures of aluminum plates made with direct current only. (*a*) Plated surface perpendicular to x-ray beam; (*b*) plated surface parallel to x-ray beam.

Improvement in Adherence

Along with the change in appearance there was also a marked improvement in the adherence of the aluminum plates. When the root mean square value of the alternating current was in less than 1:1 ratio to the direct current there was only a very slight effect on adherence. But a 2:1 ratio was sufficient to give excellent adherence even when the plated article was later bent. This was an extremely important result of the use of alternating current. A copper wire, for example, could be plated with aluminum using superimposed alternating current and the wire then could be coiled and bent at will without producing breaks.

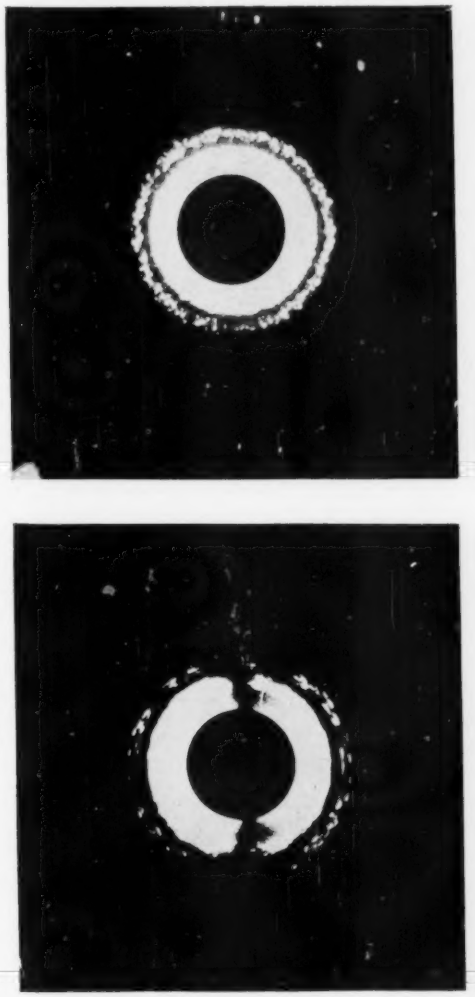

FIG. 6. X-ray diffraction pictures of aluminum plates made with a-c(rms)/d-c ratio = 2. (*a*) Plated surface perpendicular to x-ray beam; (*b*) plated surface parallel to x-ray beam.

X-Ray Examination

Transmission type x-ray diffraction photographs were taken of specially prepared plates from oper-

ations both with direct current only and with alternating current superimposed on direct current. The desired types of plates were deposited on flat copper sheets and the deposit on one side of the sheet was then carefully sanded off to expose the copper base which was dissolved in concentrated nitric acid. A thin slice about 2 mm wide was placed in a flat type Phillips x-ray camera. Two strong aluminum lines (rings) were obtained on the film in addition to a weak third line.

Fig. 5*a* and 5*b* represent x-ray diffraction pictures of aluminum plates made with direct current only. For Fig. 5*a*, the sample was mounted with the plating surface perpendicular to the x-ray beam. The uniform distribution of scattered light intensity in each ring indicates the very minute size of the aluminum crystallites. For Fig. 5*b*, the sample was mounted with the plating surface parallel to the x-ray beam. Here noticeable orientation in the aluminum plate is indicated by the nonuniform distribution within each ring.

Fig. 6*a* and 6*b* represent x-ray diffraction pictures of aluminum plates made with alternating current superimposed on the same amount of direct current as used for the d-c plate shown in Fig. 5. For Fig. 6*a* the plating surface was perpendicular to the x-ray beam and for Fig. 6*b* it was parallel. The large, approximately uniformly distributed spots in each ring indicate large, nonoriented aluminum crystallites to be present in plates made in this way. It appears that one function of the alternating current is the recrystallization of small particles deposited during the current flow in two directions, i.e., the smallest particles appear to have been selectively redissolved during the period when the reverse current was flowing. The absence of the weak third ring when the beam is parallel to the sample is attributable to the much smaller size of the target presented to the beam.

Increase in Optimum Direct Current Density

With a plating bath for which the maximum current density for good plates was 0.54 amp/dm^2 the direct current could be increased to 1.0 amp/dm^2 or higher, a 100 per cent increase. Many such tests were made but this illustrates the extent to which the operation may be pushed by superimposing alternating current.

Increase in Possible Thickness of Plates

With direct current alone very thick plates were found to be less uniform and tended to crack. By superimposing an alternating current during the plating operation it was found that the thickness of the plate could be increased several fold without producing any nonuniformity of the plate. These thick plates have absolutely no pinholes and, therefore, should offer complete protection to iron or other metal under-surfaces. The data also indicated that a higher a-c/d-c ratio is required as the desired thickness of the plate is increased. The reason is that the brittleness of the plates normally increases with increase in thickness. Clean, white plates as thick as 0.03 mm which did not crack readily were prepared but this does not represent the maximum possible.

Cathode Current Efficiencies

The use of alternating current gives cathode efficiencies which are the same as those for direct current alone. There may be, if anything, a slight increase in efficiency for the higher a-c/d-c ratios.

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Any discussion of this paper will appear in a Discussion Section, to be published in the December 1951 issue of the Journal.

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